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THE REARRANGEMENT OF ALLYLIC ARENESULFINATES

BY

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A THESIS

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ABSTRACT

Allyl, crotyl, α -methylallyl, racemic and optically active α,δ -dimethylallyl, cinnamyl and α -phenylallyl 2,6-dimethylbenzenesulfonates have been synthesized, and their reaction under various conditions examined.

In buffered acetic acid, anhydrous and aqueous ethanol, aqueous dioxane and a number of non-hydroxylic solvents, these esters have been found to undergo rearrangement to sulfone readily, in greater than 70% yield. In aqueous hydroxylic solvents the rearrangement to sulfone was accompanied by the development of small fractions of acid and the formation of small amounts of solvolysis products.

The rearrangement of the unsymmetrically substituted allylic 2,6-dimethylbenzenesulfonates to sulfones has been found to involve simultaneous isomerization of the allylic group. Similarly, optically active α,δ -dimethylallyl 2,6-dimethylbenzenesulfonate rearranged to the corresponding optically active sulfone with inversion of configuration.

A kinetic study of the rearrangement reaction has been carried out. The order of reactivity of the various 2,6-dimethylbenzenesulfonates is as follows:

allyl < crotyl < α -methylallyl \approx cinnamyl < α,δ -dimethylallyl < α -phenylallyl. This sequence is consistent with a polar transition state. However, the magnitude of the effect of a methyl or phenyl substituent on the rate of rearrangement of allyl 2,6-dimethylbenzenesulfonate in 60% ethanol-water, is much

smaller than that for the ionization of allylic chlorides (8).

The effect of variation of solvent ionizing power on the rearrangement rate has been examined. The rearrangement of the allylic 2,6-dimethylbenzenesulfinates is much less sensitive to solvent ionizing power than the ionization of p-methoxyneophyl p-toluenesulfonate (18). However, the solvent sensitivity parameter (a value, Ref. 18) is larger in the case of cinnamyl 2,6-dimethylbenzenesulfinate than in the case of the corresponding allyl ester.

The chemical behaviour of benzyl 2,6-dimethylbenzenesulfinate has also been investigated for comparative purposes. Under conditions favourable for complete rearrangement of allyl 2,6-dimethylbenzenesulfinate to sulfone, this ester underwent slow sulfur-oxygen bond fission. A comparison of the rate constants of the two reactions would indicate that the rate of rearrangement of allyl 2,6-dimethylbenzenesulfinate to sulfone is much faster than that expected from an ionization mechanism.

The bearing of the results obtained on the mechanism of rearrangement of allylic 2,6-dimethylbenzenesulfinates to the corresponding sulfones is discussed.

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INTRODUCTION

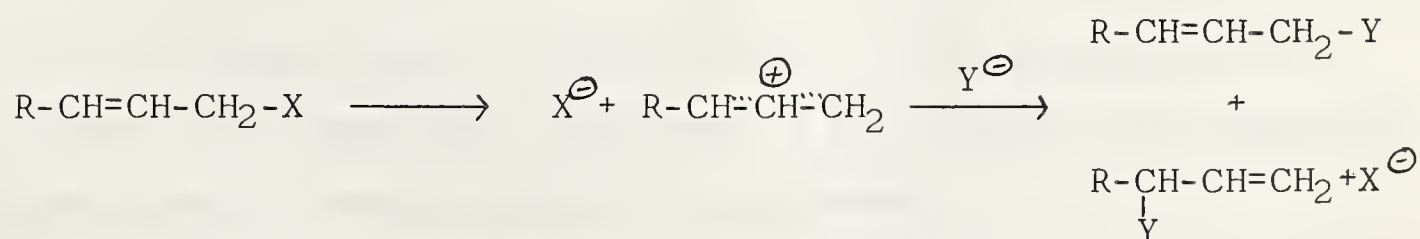
Substitution and rearrangement reactions of allylic compounds have been studied by many authors, and a review on this subject by De Wolfe and Young⁽¹⁾ appeared in 1956. As these authors point out: "allylic compounds are of theoretical interest because of their high reactivity and the ease with which they undergo rearrangement reactions". The rearrangement reactions under consideration involve the migration of electronegative substituents from C₁ to C₃ and are known as anionotropic or allylic rearrangements. Such rearrangements may take place during substitution reactions in which one electronegative functional group is replaced by another one, or in isomerization reactions in which the original functional group migrates from one end of the allylic system to the other. Reactions of the latter type involving the isomerization of allylic alcohols, esters and ethers were reviewed by Braude⁽²⁾ in 1950. There is still another type of isomerization in which both the functional group and allylic system undergo rearrangement at the same time. Reactions of this type are the Claisen rearrangement of allyl aryl ethers to allylphenols⁽³⁾, the isomerization of allylic thiocyanates to isothiocyanates⁽⁴⁾, the isomerization of allylic thionbenzoates to thiolbenzoates⁽⁵⁾, and that of allylic arylsulfinates to the corresponding sulfones⁽⁶⁾.

Allylic rearrangements can be detected only with unsymmetrically substituted compounds and with symmetrical ones which are either optically active due to an asymmetric C₁ or isotopically labeled at that carbon atom. The occurrence and

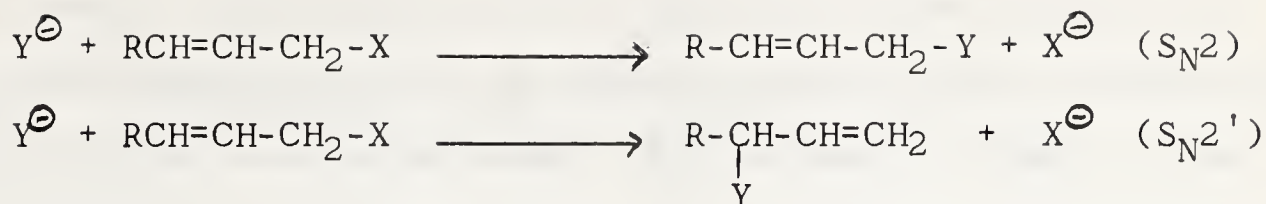
extent of this rearrangement depend largely on the substitution of the allyl radical, the nature of the functional group, and on the reaction conditions. A few examples extracted from the literature are presented below.

Allylic halides are more reactive than the corresponding saturated halides in both bimolecular and unimolecular nucleophilic substitution reactions. For example, Vernon(7) has found that at 44.6° allyl chloride undergoes bimolecular substitution by ethoxide ion in ethanol 37 times faster than n-propyl chloride. This enhancement in rate, though incompletely understood, was attributed to the stabilization of the transition state by tautomeric release of electrons from the allylic double bond to the substituted carbon atom. Vernon(8) also showed that the unimolecular reactivity of allyl chloride in 0.5% aqueous formic acid at 100° is greater by a factor of 25 than that of n-propyl chloride. The acceleration in rate in this case is clearly due to the resonance stabilization of the intermediate carbonium ion.

Allylic halides undergoing nucleophilic substitution by way of the unimolecular mechanism, S_N1, involving an intermediate mesomeric carbonium ion should yield a mixture of two isomeric products as illustrated below:



Allylic rearrangement and distribution of products may also result if the normal bimolecular substitution, S_N2, is accompanied by simultaneous abnormal substitution, S_N2'



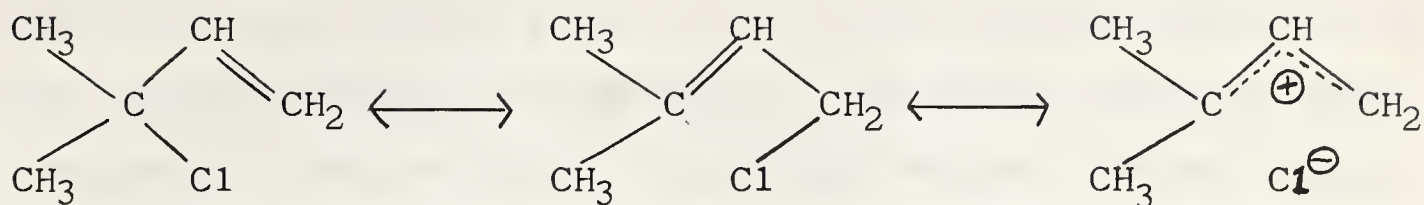
Catchpole and Hughes(9), found that in the first-order ethanolysis of α -methylallyl chloride, 82% of ethyl crotyl ether was obtained. Substrate as well as products did not isomerize under the reaction conditions. The rearranged product could not have resulted from S_N2' attack by ethanol, since they found that under similar conditions the stronger nucleophile ethoxide ion gave only normal substitution products. Similarly, Young and Andrews(10), found that on hydrolysis of α -methylallyl chloride in the presence of silver oxide a mixture of the two isomeric alcohols was obtained, of which 33.8% was crotyl alcohol.

A common intermediate for two isomeric halides in substitution reactions by a unimolecular mechanism would imply that the composition of the product mixture be identical in the two cases. This situation is actually observed only under conditions of high ionizing power and low nucleophilicity of the medium, as well as in the presence of electrophilic catalysts such as silver ion. In those cases in which different mixtures are obtained, there is somewhat more of the primary product formed from the primary reactant, a fact which can probably be explained by partial direct displacement.

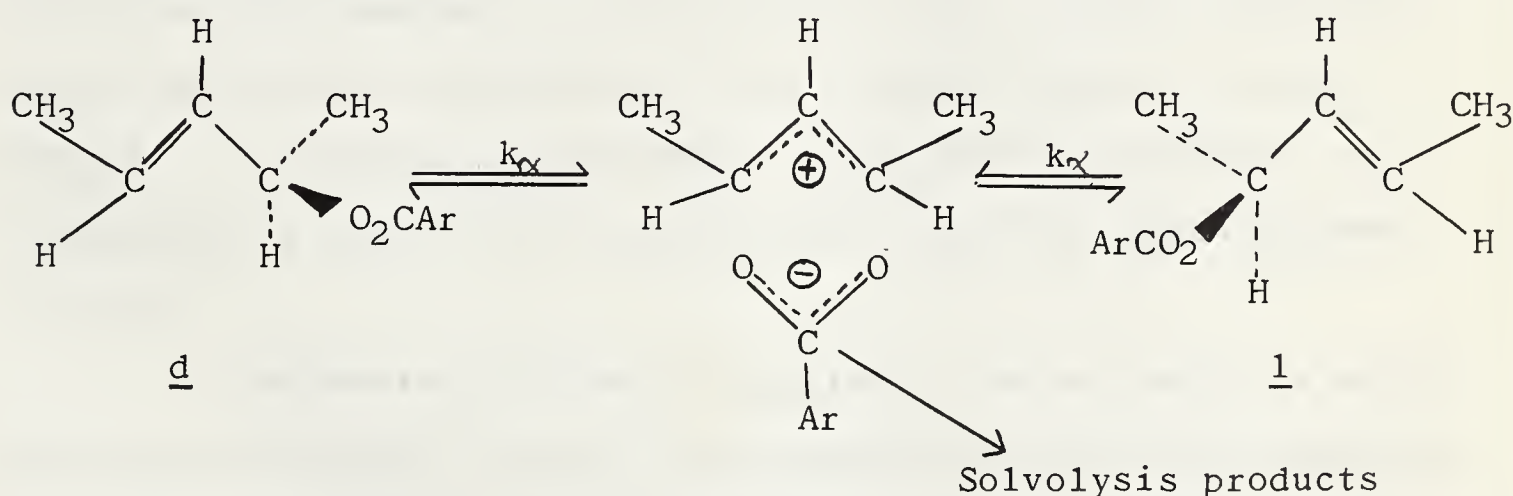
Hughes(11), who predicted the abnormal bimolecular mechanism, S_N2' , in 1938, considered the results obtained with the displacement by ethoxide ion on α -methylallyl chloride as evidence for the nonexistence of such a mechanism(9). However, further investigation of this problem including some work by

Hughes and co-workers(12), has proved the initial prediction to be correct. For example, the second-order substitution of α -t-butylallyl chloride by ethoxide ion in ethanol leads exclusively to the rearranged ethyl γ -t-butylallyl ether. This difference of reactivity between α -methylallyl and α -t-butylallyl halides toward ethoxide ion is undoubtedly a result of steric effects. The normal bimolecular mechanism, S_N2 , which operates in the case of α -methylallyl chloride becomes so slow with the α -t-butylallyl compound, that an alternative mechanism may come into play.

Of special interest are the results obtained by Young, Winstein and Goering(13), in the acetolysis of α,α -dimethylallyl chloride, since they provide the first reported evidence of ion-pair intermediates and ion-pair return in solvolysis reactions. This allylic halide undergoes simultaneous solvolysis and intramolecular isomerization to the primary γ,γ -dimethylallyl chloride, as shown by a downward drift of the rate constant to a value corresponding to the primary halide and the isolation of rearranged compound after 30% reaction. Common ion rate depression was not observed upon addition of chloride ion to the reaction solution. On the basis of this and former evidence, it was suggested that the allylic rearrangement of α,α -dimethylallyl chloride to γ,γ -dimethylallyl chloride took place by an "internal return" from an ion pair intermediate. The transition state was considered as a hybrid of the following resonance structures:



Internal return was also detected by Goering(14) in his extensive studies of allylic carboxylic esters. He found, for example, that in the solvolysis of optically active α, δ -dimethylallyl p-nitrobenzoate in 90% aqueous acetone at 100°, the optical activity disappears completely and the polarimetric rate (k_α) is five times larger than the titrimetric rate (k_t). Since the ratio of k_α/k_t is not affected by the addition of a common-ion salt and no exchange has been observed, it has been concluded that no "external return"(15) takes place. Therefore, the excess racemization ($k_{rac}=k_\alpha-k_t$) represents internal return and is completely intramolecular and stereospecific. The reaction scheme is as follows:



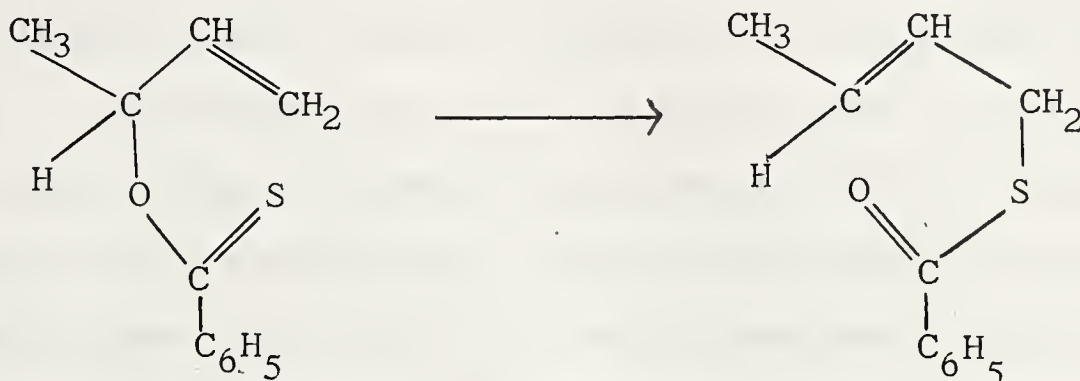
It was also found that in both 60 and 90% aqueous acetone, carbonyl- O^{18} α, δ -dimethylallyl p-nitrobenzoate undergoes equilibration of the label between the carbonyl and ether positions at an equal rate to that of racemization, i.e., $k_{eq}=k_{rac}$.

This indicates that both the carboxyl oxygen atoms in the anion and the allylic carbon atoms in the cation become equivalent in the intimate ion-pair intermediate. The polar nature of this intermediate was definitely established by the observed sensitivity of all mentioned rates to ionizing power of the medium. A more subtle aspect on the nature of the intermediate regarding the question whether both oxygen atoms are equivalent with respect to both carbon atoms or not, has also been investigated by these authors. This was performed by the use of an O^{18} labeled optically active ester and by locating the label in each enantiomer of the racemized unsolvolyzed ester. The results obtained indicate that the oxygen atoms of the ion pair react with the nearest carbon atom 3.8 times faster than with the more remote one in 60% aqueous acetone and 4.9 times faster in 90% aqueous acetone. With another p-nitrobenzoate ester, that of α -phenylallyl alcohol, it was shown by Braude and Turner (16), that the intramolecular rearrangement of this ester to the cinnamyl ester results in complete conversion of the carbonyl oxygen to ether oxygen. The conclusion was based on the results obtained from experiments carried out on carbonyl- O^{18} ester in chlorobenzene at 130° .

As Winstein (17) has recognized, one may expect a whole spectrum of merging ion-pair and non-ionic cyclic rearrangements.

There are recent reports on several allylic type compounds for which rearrangement reactions involve very little change in charge separation between the ground and transition state, as evidenced by low sensitivity of rate to solvent ionizing power and substituent effect.

Allylic thionbenzoates were found by Smith(5), to undergo thermal rearrangement to thiolbenzoates. From the fact that α -methylallyl thionbenzoate is converted to crotyl thiolbenzoate, it follows that in this case there is a simultaneous allylic and functional group rearrangement.



From the kinetic data of rearrangement of allyl, α -methylallyl and crotyl thionbenzoates in a number of solvents, it was shown that the reaction is little sensitive to solvent polarity. For example, the rate in acetic acid is only ten times faster than it is in cyclohexane. The relative rate between acetic acid and tetrahydrofuran is smaller by three powers of ten than in the ionization of p-methoxyneophyl tosylate(18). The order of reactivity of the three compounds is allyl < crotyl < α -methylallyl, which is as expected from an ionic reaction. However, the acceleration in rate produced by the methyl group is much smaller than in the solvolysis of allylic halides(8).

Although it was known for a long time that most allylic thiocyanates undergo intramolecular rearrangement on heating to isothiocyanates of inverted allylic structure(1), mechanistic studies were not available until recently.

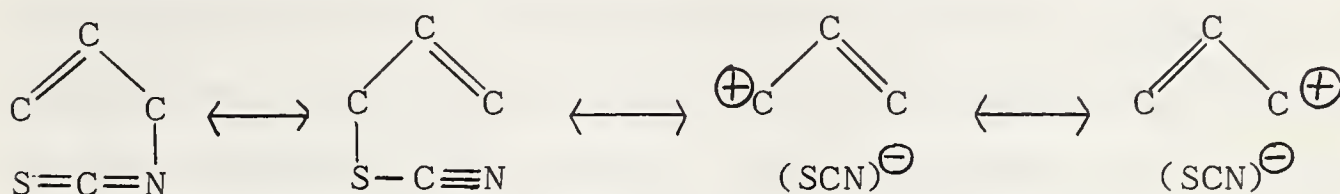
Smith and Emerson(4a), obtained kinetic data for the rearrangement of allyl thiocyanate to allyl isothiocyanate which

showed that the reaction rates in toluene, nitrobenzene and dimethylformamide were almost identical. On the basis of these results, the negative entropy of activation and the allylic shift that had been known to accompany the isomerization of crotyl thiocyanate, they suggested an intramolecular mechanism proceeding through a pseudo six-membered ring transition state.

The observations that no allylic shift takes place in the isomerization of cinnamyl thiocyanate which yields only cinnamyl isothiocyanate (19), and that the rate of this reaction is much slower than that of the allyl compound, has been considered by Smith and Emerson as evidence that an ionic mechanism operates in this case. To explain the different behaviour of cinnamyl thiocyanate, it was suggested that allylic shift could not occur in this case because it would have converted the conjugated cinnamyl group into the nonconjugated α -phenylallyl group.

Iliceto, Fava and Mazzucato (4b) studied the kinetics of isomerization of allyl, crotyl and α,δ -dimethylallyl thiocyanates to the corresponding isothiocyanates of inverted structure, in the solvents acetonitrile and cyclohexane at 60°. They found that the order of reactivity was: allyl < crotyl < δ , δ -dimethylallyl. However, as in the case of the thionbenzoates, the variation in rate with substitution is much too small in comparison with that observed in the ionization of allylic halides (8). The difference in rate between the two solvents was very small and with allyl and crotyl the reaction was even faster in the less polar solvent, cyclohexane.

The representation of the transition state which was suggested by these authors resembles that given by Young, Winstein and Goering(13) for the rearrangement of α, α -dimethylallyl chloride, and is shown below:



Of interest is the reported evidence in support of the fact that during this isomerization an equilibrium is established, in which substantial amounts of thiocyanate are present.

On account of this evidence it is suggested by the authors that the failure to detect any α -phenylallyl isothiocyanate in the isomerization of cinnamyl thiocyanate may be explained in terms of reaction equilibrium. The stabilization energy due to conjugation which is present in the cinnamyl thiocyanate may shift the equilibrium toward this compound to the extent that only very small amounts of α -phenylallyl isothiocyanate are present.

The rearrangement of allylic azides studied by Gagneaux, Winstein and Young(20), is probably the best example of very low sensitivity of reaction rate to substituent and solvent effects. For example, the rate of isomerization of α, α -dimethylallyl azide is only 3-4 times larger than that of α -methylallyl azide, and a change in solvent from pentane to 70% aqueous acetone causes an increase in rate of only one power of ten. In this isomerization no solvolysis was detected even in 70% aqueous acetone.

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Attention is now directed to some chemical aspects of sulfinates as they appear in the literature.

As in the solvolysis of the structurally similar carboxylic esters, whereupon either acyl-oxygen or alkyl-oxygen bond cleavage may occur, the solvolysis of sulfinates may also proceed by either sulfur-oxygen or carbon-oxygen bond cleavage or by a combination of the two. The occurrence and extent of each process will depend of course, on the substrate and reaction conditions employed.

Product analysis, the use of optically active compounds and kinetic studies are among the most valuable criteria in the determination of the position of bond fission and reaction mechanism.

An unequivocal indication for sulfur-oxygen bond cleavage in the alcoholysis of sulfinates is the production of the parent alcohol and a new sulfinate ester corresponding to the alcohol used as solvent.



On the other hand, if carbon-oxygen bond fission occurs under the same conditions, the products would be sulfinic acid, ether and/or sulfone:



For example, Kenyon, Phillips and Taylor (21) found that the *p*-toluenesulfonates of purely aliphatic and hydroaromatic alcohols do not yield ethers when heated with alcohols.

Thus, ethyl p-toluenesulfinate yields only d-2-octyl and l-menthyl p-toluenesulfinate when heated respectively with d-2-octanol and l-menthol.

These authors also showed that on refluxing a solution of l-phenylmethylcarbonyl p-toluenesulfinate in ethanol with added potassium acetate or carbonate, the main product of this reaction was the optically active alcohol of unchanged rotation. The retention of configuration in this case and the formation of new sulfinate esters in the previous one, are clear evidence of sulfur-oxygen bond fission.

If however, the last experiment is repeated without addition of salt, the ethyl ether of phenylmethylcarbinol is obtained with extensive racemization. Similarly, in acetic acid, the l-sulfinate was converted into rac-phenylmethylcarbonyl acetate. These results would support alkyl-oxygen fission reactions. The formation of racemic acetate also indicates an ionization process.

Herbrandson and Cusano(22) have observed sulfur-oxygen bond fission in the ethoxide ion catalyzed ethanolysis of epimeric (-)-menthyl p-iodobenzenesulfinate. The reaction showed second-order kinetics, first-order in both ester and base, and yielded pure (-)-menthol and ethyl p-iodobenzenesulfinate.

Bunton and Hendy(23) have measured the kinetics of hydrolysis of methyl and benzhydryl p-toluenesulfinate in aqueous dioxane and determined the position of bond fission by the use of H_2O^{18} enriched solvent. The hydrolysis of the methyl ester which is very slow in neutral aqueous dioxane, is however acid catalyzed and becomes very fast under basic conditions even at 0° .

Since no incorporation of O^{18} could be detected in the isolated methanol from both acidic and alkaline hydrolyses, it was concluded that the sulfur-oxygen bond was broken during these reactions.

Similar experiments on the benzhydryl ester revealed that the second-order reaction between ester and hydroxide ion also proceeds by sulfur-oxygen cleavage since no incorporation of O^{18} in the parent carbinol could be detected. In the acid catalyzed hydrolysis however, the reaction proceeds predominantly by carbon-oxygen cleavage. The kinetic results and the isolation of small amounts of sulfone in this case, indicate that a carbonium ion mechanism is partially operative.

The difference in behaviour between methyl and benzhydryl sulfinates in acidic solution is in accord with the ability of the latter compound to produce a much more stable carbonium ion.

In a recent investigation, Noreyko(24), has examined the reaction of various p-methoxyneophyl arylsulfinates in aqueous ethanol and absolute ethanol in the presence of such bases as ethoxide ion, potassium acetate and 2,6-lutidine. The kinetic data and product analyses indicate that the solvolysis of these esters occurs with complete sulfur-oxygen cleavage. In ethanol, ethyl sulfinates and unrearranged p-methoxyneophyl alcohol are isolated in every case.

The reaction mechanism may be described as involving a rate determining bimolecular nucleophilic displacement on sulfur by the base used, which in the case of acetate ion and 2,6-lutidine is followed by a rapid decomposition of the un-

stable intermediate.

The rearrangement of sulfinic acid esters to corresponding sulfones has attracted some interest in the past.

Arcus, Balfe and Kenyon(25) observed that the rearrangement of α -phenylethyl p-toluenesulfinic acid to the corresponding sulfone was favoured by an increase in solvent polarity and susceptible to exchange. This was considered as consistent with an ionic mechanism.

In formic acid as solvent, optically active ester is converted in high yield to completely racemic sulfone. In formic acid-sodium formate solution, the yield of sulfone is drastically reduced and accompanied by an increase in yield of formate ester. The sulfone and formate ester were partially active and of retained configuration. To explain the activity and retention of configuration of the sulfone, an intramolecular rearrangement mechanism has been suggested, involving simultaneous cleavage of the carbon-oxygen bond and formation of the carbon-sulfur bond.

Wragg, McFadyen and Stevens(26) who recently investigated the rearrangement of a number of sulfinic acid esters to sulfones, suggested an intermolecular ionic mechanism for their results.

These authors found that the rearrangement occurred on heating the esters in acetic acid-HCl or in a homogeneous state. They also observed that no reaction occurred in such nonpolar solvents as benzene or toluene, unless some sulfinic acid was present. The yield of sulfone was greater and the rate faster with α,α -dimethylbenzyl than with α -methylbenzyl p-toluenesulfinic acid, while no sulfone was obtained from the reaction of either

methyl, phenyl, benzyl and o-nitrobenzyl esters. These results are consistent with a rate determining ionization process. The intermolecular character of the rearrangement was established by the production of some p-chlorophenyl diphenylmethyl sulfone in the reaction of diphenylmethyl p-toluenesulfinic acid in acetic acid containing p-chlorobenzenesulfinic acid.

Neither of the last two reports provides any information with regard to the type of ionization, i.e., dissociation to free ions or ion pairs. The recent investigation by Darwish and McLaren (27) proves quite useful in this respect.

These authors examined the solvolysis and rearrangement of t-butyl, benzhydryl, α -phenylethyl and α -(p-methoxyphenyl)-ethyl 2,6-dimethylbenzenesulfinates in a number of buffered hydroxylic solvents. In every case sulfones were formed along with solvolysis products.

The ionic character of the sulfinic acid to sulfone rearrangement was established by the observations that the rate of sulfone formation exhibits the same sensitivity to ionizing power of solvent as solvolysis, and that the enhancement in rate of α -(p-methoxyphenyl)-ethyl ester comparable to α -phenylethyl in both rearrangement and solvolysis is characteristic of ionic species. It was furthermore shown that the important route to sulfone formation is ion pair recombination and not recombination of free ions. This was established on the basis that in the presence of added 2,6-dimethylbenzenesulfinic acid ion the fraction of sulfone remains constant. Similarly no exchange to yield sulfone was observed in the solvolysis of the corresponding halides in the presence of lutidinium 2,6-dimethylbenzene-

sulfinate.

The most pertinent data with regard to the present work, was reported by Cope, Morrison and Field(6) who studied the thermal rearrangement of allyl benzenesulfonates. The esters examined by these authors were: allyl, crotyl and α -methylallyl benzenesulfonates.

From a sample of allyl benzenesulfonate which was heated for twenty nine hours at 100° without a solvent and underwent some decomposition, 70% of starting material and 20% of allyl phenyl sulfone were recovered. The sulfone was identified by hydrogenation to n-propyl phenyl sulfone.

To minimize decomposition, the other two esters were subjected to reaction in toluene solution. From a toluene solution 2M in crotyl benzenesulfonate ester which was heated for six and one-half hours at 100°, followed by removal of the solvent and saponification of unreacted ester, an 18% yield of sulfone was recovered. The identity of this sulfone was established as crotyl phenyl sulfone in the following manner: reduction of the product and subsequent nitration, reduction, and reaction of the resulting amino compound with m-bromobenzoyl bromide, gave two crystalline derivatives, n-butyl m-(3-bromobenzoylamino)-phenyl sulfone and n-butyl m-(di-3-bromobenzoylamino)-phenyl sulfone.

On treatment of α -methylallyl benzenesulfonate in a similar manner, with the exception that heating was at 80°, a 20% yield of sulfone was obtained, identified as crotyl phenyl sulfone as above. The authors also indicate that the products from the last two esters may have contained small amounts of the

isomeric α -methylallyl phenyl sulfone. No kinetic study was made in this case.

With regard to mechanism, they point out that: "the bearing of this evidence on the mechanism of the rearrangement is inconclusive. An intramolecular cyclic process would result in inversion of the crotyl and α -methylallyl groups and lead to the isomeric α -methylallyl and crotyl sulfones, unless these sulfones were interconverted at the temperature of the rearrangement".

These authors also considered an ionic mechanism proceeding through dissociation of the isomeric sulfinates to a free resonance stabilized carbonium ion and sulfinate anion, which on recombination would lead to the same product from both esters.

The results obtained by Cope, Morrison and Field⁽⁶⁾ indicated the susceptibility of allylic benzenesulfinates to undergo rearrangement to sulfones. The present investigation of allylic 2,6-dimethylbenzenesulfinates was undertaken in order to elucidate the mechanism of the sulfinate to sulfone rearrangement.

CHAPTER 1

The Rearrangement Reaction of Racemic and Optically Active α,δ -Dimethylallyl 2,6-Dimethylbenzenesulfinate

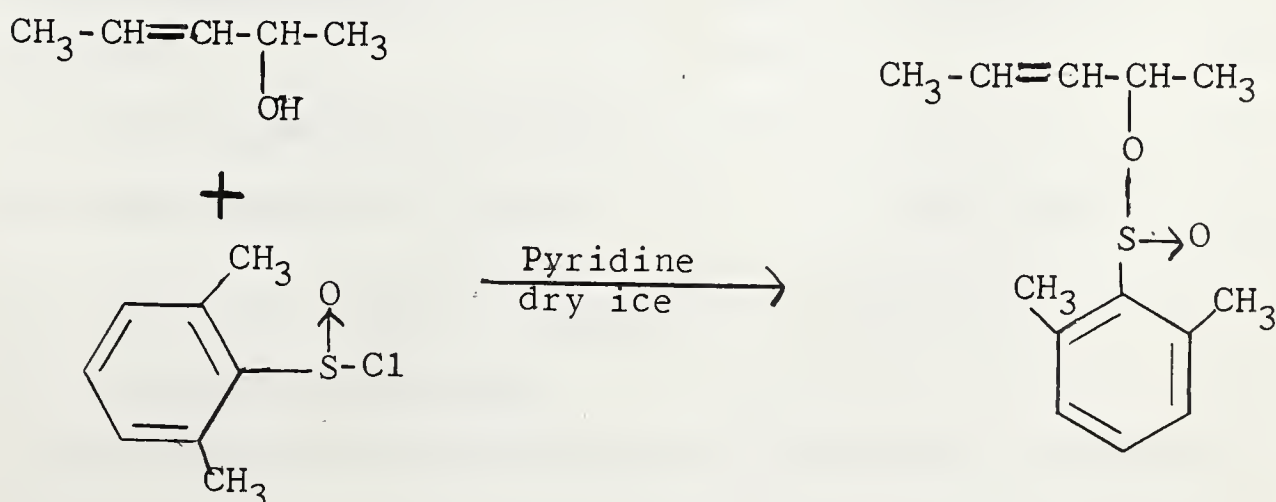
RESULTS

A. The synthesis and reactions of racemic α,δ -dimethylallyl 2,6-dimethylbenzenesulfinate.

α,δ -Dimethylallyl alcohol was obtained by treatment of crotonaldehyde with methylmagnesium iodide.

The preparation of 2,6-dimethylbenzenesulfinic acid was carried out according to the method used by Hanke(28) for the preparation of *p*-chlorobenzenesulfinic acid. Diazotization of 2,6-dimethylaniline and subsequent treatment of the diazonium salt with sulfur dioxide in the presence of copper powder, gave the desired sulfinic acid.

2,6-Dimethylbenzenesulfinic acid was converted to the corresponding sulfinyl chloride by treatment with thionyl chloride, and treatment of this compound with α,δ -dimethylallyl alcohol in pyridine in a dry ice-acetone bath, afforded α,δ -dimethylallyl 2,6-dimethylbenzenesulfinate ester.



If the solution was not adequately cooled, the sulfinate ester was contaminated with 2,6-dimethylphenyl 2,6-dimethylbenzenethiosulfonate. The presence of this compound can be detected by its infrared spectrum (strong band at 1335 cm^{-1} in CS_2), and melting point ($123-125^\circ$). Similarly, if all the excess thionyl chloride was not removed from the 2,6-dimethylbenzenesulfinyl chloride, the α,δ -dimethylallyl 2,6-dimethylbenzenesulfinate was contaminated with the corresponding sulfite ester. The sulfite ester gives rise to a strong doublet at $1200-1220\text{ cm}^{-1}$ (CS_2), a region in which the 2,6-dimethylbenzenesulfinate shows essentially no absorption.

Some characteristic properties of α,δ -dimethylallyl alcohol, 2,6-dimethylbenzenesulfinate and 2,6-dimethylphenyl sulfone are summarized in Table I.

TABLE I
Physical Properties of α,δ -dimethylallyl alcohol,
2,6-dimethylbenzenesulfinate and 2,6-dimethylphenyl
sulfone^a.

α,δ -Dimethylallyl	n_D^{25}	M.p., $^\circ\text{C}$.	IR absorption ^b cm^{-1}
Alcohol	1.4260	-	3605
2,6-Dimethylbenzenesulfinate	1.5353	-	1130, 840
2,6-Dimethylphenyl sulfone	-	56.0-58.0	1310, 1145

a - The n.m.r. data are reported in Table XI

b - In carbon disulfide.

α,δ -Dimethylallyl alcohol and α,δ -dimethylallyl 2,6-dimethylbenzenesulfinate showed absorption in the infrared at 965(s) and 960 cm^{-1} , respectively, in carbon disulfide. On this basis, both compounds were assigned a trans configuration at the olefinic double bond (29). Bellamy(30) reports that sulfinate esters give rise to an intense infrared band at 1126-1136 cm^{-1} .

A series of preliminary studies on the reaction of α,δ -dimethylallyl 2,6-dimethylbenzenesulfinate were carried out by heating or refluxing this compound (0.02-0.03 M) in various solvents, containing 0.04-0.05 M acetate salt which acted as a buffer to prevent catalysis by strong acid. The reaction products were extracted with ether, and residues obtained after evaporation of the ether were identified by infrared spectroscopy. In all the experiments carried out the infrared spectral data indicated complete disappearance of the sulfinate ester and formation of sulfone. The reaction conditions and yields of sulfone are summarized in Table II.

The sulfone which was recovered from the run in acetic acid, was contaminated with traces of acetate as evidenced by a very weak band in the infrared spectrum at 1730 cm^{-1} . The sulfone obtained from the run in 80% ethanol-water was contaminated with traces of alcohol, as evidenced by a very weak infrared band at 3600 cm^{-1} . There was no infrared evidence for the formation of solvolysis products in the runs using 80 and 90% dioxane-water or anhydrous ethanol as solvent. The upper limits for percent solvolysis in the various solvents, as determined by the amounts of acid produced during more than 10

TABLE II

A summary of yields of α,δ -dimethylallyl 2,6-dimethylphenyl sulfone from the reaction of α,δ -dimethylallyl 2,6-dimethylbenzenesulfinate.

Solvent	Time, hr.	$t_{1/2}$ ^a , hr.	Temp., °C.	(Ester), M	(Base), M	Sulfone, % yield
AcOH	12	0.1	80	0.0246	0.0454 ^c	70.2
EtOH	32	0.4	78	0.0220	0.0481 ^d	82.5
80% EtOH-water	44	- ^b	80	0.0253	0.0488 ^c	83.9
80% Dioxane-water	168	0.3	90	0.0233	0.0416 ^e	85.1
90% Dioxane-water	168	0.6	90	0.0245	0.0416 ^e	75.5

a - Approximate values at 70.07°.

b - In 90% EtOH-water at 70.07°, $t_{1/2}$ = ca. 0.2hr.

c - NaOAc; d - KOAc; e - Bu₄NOAc.HOAc.

half-lives, are as follows: acetic acid - 7.2%, 80% ethanol-water - 3.5%, 80 and 90% dioxane-water - 2.2% each (Table III). In anhydrous ethanol at 70°, with added 2,6-lutidine, no acid was produced (Table III), and accordingly no solvolysis of the ester occurred. There was no infrared evidence for the formation of ethyl 2,6-dimethylbenzenesulfinate in the run using anhydrous ethanol as solvent. This compound, if formed, could have been detected by its strong infrared absorption in carbon disulfide solution at 882 cm⁻¹ (Chapter 2), since the sulfone showed essentially no absorption at that frequency.

The sulfone was crystallized from pentane, and positively identified as α,δ -dimethylallyl 2,6-dimethylphenyl

sulfone by infrared and n.m.r. spectra, and C,H,S analysis. In the infrared, the sulfone showed strong absorption at 1145 and 1310 cm^{-1} (Table I). Bellamy(30) reports that sulfones give rise to two strong bands in the infrared at 1160-1120 and 1350-1300 cm^{-1} . A trans configuration was assigned at the olefinic double bond of the sulfone, on the basis of an infrared band at 960 cm^{-1} in carbon disulfide solution (29).

Titrimetric control runs to measure the amount of acid developed at various time intervals, were also carried out. The purpose of this was to determine the extent solvolysis accompanying rearrangement.

TABLE III

A summary of titrimetric results for the reaction of α,γ -dimethylallyl 2,6-dimethylbenzenesulfinate under various conditions.

Solvent	Temp., °C.	(Ester), M	(Base), M	Time, hr.	% Acid formed
AcOH	80	0.0246	0.0454 ^a	12	7.2
EtOH	70	0.0215	0.0406 ^b	4 ^d	0.0
80% EtOH-water	80	0.0223	0.0503 ^a	2 41	3.5 14.2
60% EtOH-water	90	0.0221	0.0509 ^a	0.12 ^d	4.7
60% EtOH-water	70	0.0215	0.0406 ^b	0.5 ^d	1.3
80% Dioxane-water	90	0.0228	0.0443 ^c	2 143	2.2 19.8
90% Dioxane-water	90	0.0231	0.0443 ^c	12 141	2.2 23.9

a - NaOAc; b - 2,6-Lutidine; c - $\text{Bu}_4\text{NOAc} \cdot \text{HOAc}$.

d - These values correspond to approximately 10 half-lives as determined by the infrared kinetic measurements; all the other time values are in excess of 10 $t_{1/2}$.

The runs in anhydrous ethanol and 60% ethanol-water listed in Table III, were carried out after the kinetic data obtained by the infrared method had been available. The other runs were carried out before such data was available. As indicated by the data of Table III, no acid was produced during the reaction of α,δ -dimethylallyl 2,6-dimethylbenzenesulfinate in anhydrous ethanol with added 2,6-lutidine, while in 60% ethanol-water, 4.7 and 1.3% acid were produced in the presence of sodium acetate and 2,6-lutidine, respectively. In all the other runs listed in Table III, the samples which were titrated had been heated for time periods exceeding the time required for complete rearrangement of the ester, as later determined by the infrared kinetic method. Accordingly, the titrimetric results obtained in acetic acid, 80% ethanol-water, 80 and 90% dioxane-water do not provide definite information with regard to the extent solvolysis of the sulfinate ester. However, the data may be used to determine the upper limits for the extent of ester solvolysis (p.20). Some of the acid produced in these solvents may be due to side reactions, occurring during the prolonged heating of the solutions.

In addition to the reactions reported in Table II, the reaction of α,δ -dimethylallyl 2,6-dimethylbenzenesulfinate in n-octane with added anhydrous sodium carbonate as a second phase, was also studied. In this case, a yield of 83.3% of α,δ -dimethylallyl 2,6-dimethylphenyl sulfone was obtained after heating on a steam bath for 27 hours, and subsequent filtration and evaporation of the solvent under vacuum at room temperature..

B. The synthesis, reaction and kinetics of optically active α,δ -dimethylallyl 2,6-dimethylbenzenesulfinate.

The resolution of α,δ -dimethylallyl alcohol was accomplished by the method described by Hills, Kenyon and Phillips(31) and by Alexander and Kluiber(32), which involved a multi-step process.

α,δ -Dimethylallyl alcohol was converted to α,δ -dimethylallyl acid phthalate by heating with phthalic anhydride in pyridine. To a warm solution of the racemic acid phthalate in a 2:1 mixture of acetone-chloroform, an equivalent amount of brucine was added. On cooling the (-)-brucine salt of (+)- α,δ -dimethylallyl acid phthalate crystallized out.

This compound was then hydrolyzed with 4N hydrochloric acid solution, yielding (+)- α,δ -dimethylallyl acid phthalate. Treatment of the active acid phthalate with 8N NaOH solution, afforded the desired compound, (+)- α,δ -dimethylallyl alcohol, $\alpha_D^{25} = 0.261 \pm 0.007^\circ$ ($l = 1$, neat). Alexander and Kluiber(32) report $\alpha_D^{25} = 0.07 \pm 0.02^\circ$ ($l = 1$, neat) and $\alpha_D^{25} = 0.16 \pm 0.02^\circ$ ($l = 1$, neat) for two crops of (+)- α,δ -dimethylallyl alcohol, obtained by the method described above. Hills, Kenyon and Phillips(31) report that the optical rotation of (+)- α,δ -dimethylallyl alcohol is very sensitive to temperature. One sample of this alcohol, for example, is reported to be dextrorotatory at 20° , $\alpha_D^{20} = 0.50^\circ$ (neat) and levorotatory at 30° , $\alpha_D^{30} = -0.16^\circ$ (neat).

(+)- α,δ -Dimethylallyl alcohol was converted to (+)- α,δ -dimethylallyl 2,6-dimethylbenzenesulfinate by treatment

with 2,6-dimethylbenzenesulfinyl chloride in pyridine, in a dry ice-acetone bath.

The active sulfinic acid ester, a liquid, had a specific rotation of $[\alpha]_D^{25} + 3.86^\circ$ ($l = 1$, $c = 5$, ethanol), and was positively identified as sulfinic acid by comparing its infrared spectrum with that of the racemic compound. The ester was assigned a trans configuration on the basis of an infrared band at 960 cm^{-1} (CS_2).

To obtain some information about the behaviour of the (+)- α,δ -dimethylallyl 2,6-dimethylbenzenesulfinate, a solution of this compound in anhydrous ethanol with added sodium acetate, was heated in sealed tubes at 70.07° and the change of rotation with time was observed.

The specific rotation of such a solution, which was $+1.18^\circ$ at zero time, decreased gradually to a minimum of -11.90° after 30 minutes and then, more slowly, increased again to a maximum value of $+7.95^\circ$ after 245 minutes, remaining constant thereafter.

These results which were obtained in several runs, using either sodium acetate or 2,6-lutidine as buffers, are consistent with the diastereomerism of the active sulfinic acid ester. This diastereomerism is due to the additional asymmetric centre, at the sulfur atom, and is a well known phenomenon of active sulfinates. As a result, two diastereomers i.e., (+)(+) and (+)(-), of opposite signs of rotation and different reaction rates were present in the starting material. In this case, the diastereomer of positive rotation reacted faster than the other one.

To verify that the negative rotations were due to ester, a solution of (+)- α,δ -dimethylallyl 2,6-dimethylbenzenesulfinate (0.0473M) in anhydrous ethanol, in the presence of 2,6-lutidine (0.0520M), was heated for 30 minutes at 70.07°. The sulfinate ester which was isolated after this time from the reaction mixture, had a specific rotation of $[\alpha]_D^{25} -24.30^\circ$ ($l = 4$, $c = 1.76$, ethanol). The identity of this compound was confirmed by its infrared spectrum, which also showed slight contamination with sulfone.

In another experiment, a solution of (+)- α,δ -dimethylallyl 2,6-dimethylbenzenesulfinate (0.0504M) in anhydrous ethanol with added sodium acetate (0.0503M), was divided in two equal portions. The sulfone isolated from one portion which was heated for 30 minutes at 70.07°, had a specific rotation $[\alpha]_D^{25} +6.44^\circ$ ($l = 4$, $c = 1.28$, ethanol), and the sulfone isolated from the other portion which was heated for 23 hours at 70.07° had a specific rotation, $[\alpha]_D^{25} +7.05^\circ$ ($l = 4$, $c = 1$, ethanol).

Thus the sulfone that is formed is optically active and similar in sign and degree of rotation in both cases.

The fact that the specific rotation of the isolated sulfone (+ 7.05°) was identical to that of the sulfinate ethanolic solution after 240 minutes at 70.07° (7.06°, average of three runs), would indicate quantitative rearrangement of sulfinate to sulfone, provided that no other optically active products were present.

Plotting $\log([\alpha]_{D,\infty}^{25} - [\alpha]_{D,obs.}^{25})$ vs. time, a curve was obtained, with the points related to the slow reacting diastereomer lying on a straight line (Fig. 1). By extra-

polation of this line to zero time, $\log([\alpha]_{D,\infty}^{25} - [\alpha]_{D,0}^{25})$ was obtained. From this value, the theoretical specific rotation of the slow reacting diastereomer, of negative sign of rotation, could be calculated; $[\alpha]_{D,0}^{25} -37.75^\circ$. The data used for this plot (Fig. 1) and the calculations for the determination of the rate constant for the slow reacting diastereomer, from the first-order kinetic expression shown below, appear in Table IV.

$$k = \frac{2.303}{t} \log([\alpha]_{D,\infty}^{25} - [\alpha]_{D,0}^{25}) / ([\alpha]_{D,\infty}^{25} - [\alpha]_{D,0}^{25} \text{ obs.})$$

C. Kinetic data for the rearrangement of racemic sulfinate to sulfone obtained by the infrared method.

In order to follow the rate of disappearance of α,δ -dimethylallyl 2,6-dimethylbenzenesulfinate by infrared measurements, it was necessary to find a characteristic ester band in a region free of interference from sulfone. An absorption band at 11.85 microns was selected for this purpose. Before this band could be used for rate calculations, a control run on the adherence of the optical absorption of the ester in this region to the Lambert-Beer law, as well as on the extraction procedure was carried out in the following manner. A standard solution of the sulfinate ester (0.0259 M) in anhydrous ethanol was prepared. Aliquots of this solution were diluted with anhydrous ethanol, using the same automatic pipette, so that the concentrations of the new solutions were known fractions of the original one. A five ml. aliquot from each solution, including the original one, was extracted with pentane and washed with several portions of water in a uniform manner. The residue obtained by evaporation of the solvent, was

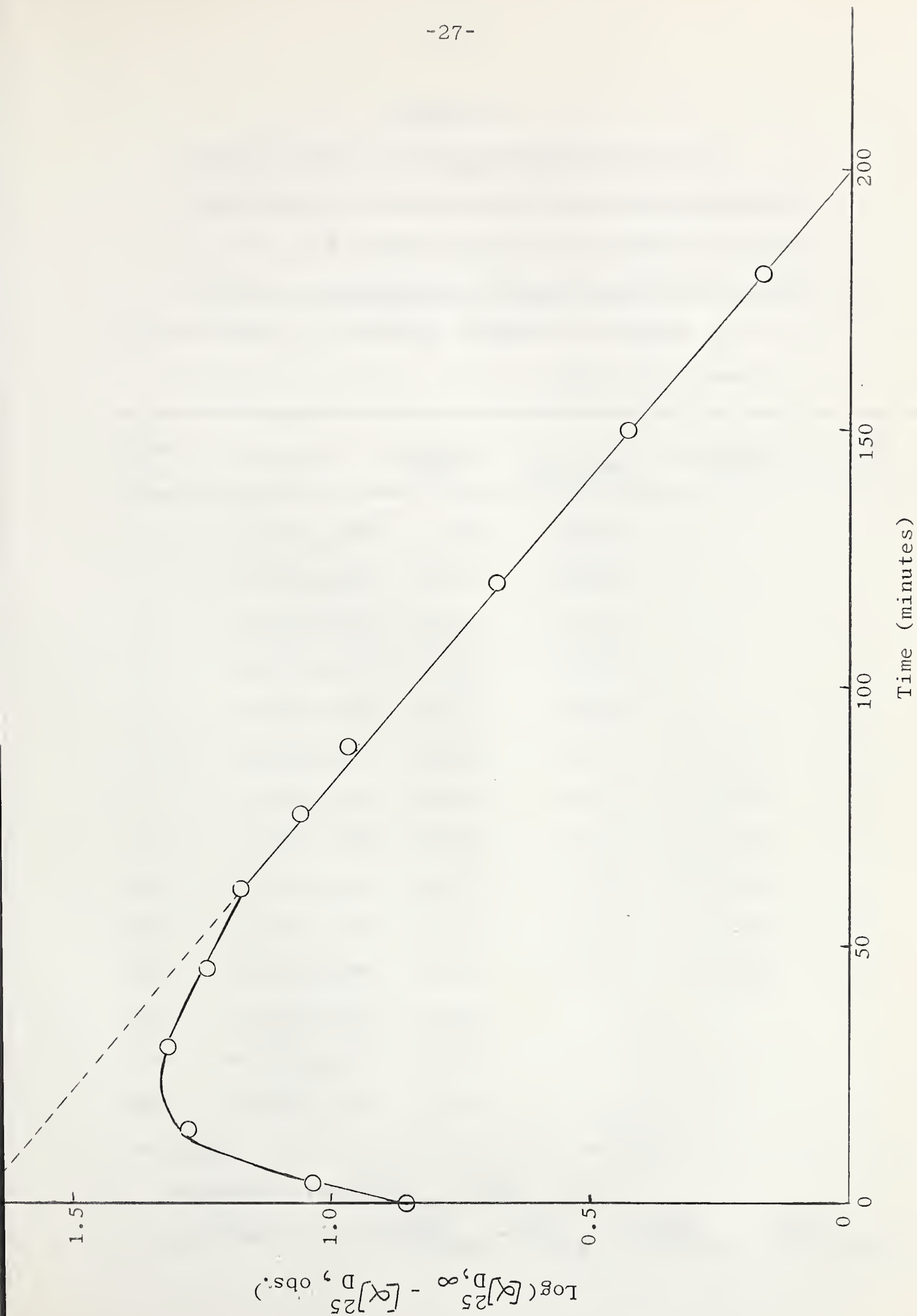


Fig. 1. Plot of polarimetric data for the rearrangement of (+)- α, δ -dimethylallyl 2,6-dimethylbenzenesulfonate to (+)- α, δ -dimethylallyl 2,6-dimethylphenyl sulfone in anhydrous ethanol at 70.07° (Table IV).

TABLE IV

Calculations for the determination of the
polarimetric rate constant in the rearrangement
of (+) - α,γ -dimethylallyl 2,6-dimethylbenzene-
sulfinate in anhydrous ethanol at $70.07 \pm 0.02^\circ$.

Run #3 (Ester) = 0.0504M; (NaOAc) = 0.0503M; $\underline{1} = 4$,

$\underline{c} = 1.2$, ethanol

Time, min.	α_D^{25}	$[\alpha]_D^{25}$	$\text{Log}(a-x)^*$	$\text{Log}\left(\frac{a}{a-x}\right)^*$	$k \times 10^4$ sec^{-1}
0	$+0.057 \pm .004^\circ$	$+1.18^\circ$	0.8306		
5	$-0.117 \pm .005$	-2.43	1.0161		
15	$-0.501 \pm .002$	-10.43	1.2644		
30	$-0.571 \pm .004$	-11.90	1.2978		
45	$-0.433 \pm .005$	-9.02	1.2297		
60	$-0.316 \pm .005$	-6.58	1.1623	0.4976	3.18
75	$-0.155 \pm .008$	-3.22	1.0479	0.6120	3.13
90	$-0.043 \pm .0005$	-0.89	0.9465	0.7134	3.04
120	$+0.153 \pm .005$	$+3.18$	0.6785	0.9814	3.14
150	$+0.253 \pm .005$	$+5.27$	0.4281	1.2318	3.10
180	$+0.312 \pm .008$	$+6.50$	0.1614	1.4985	3.19
245	$+0.382 \pm .006$	$+7.95$			
1440	$+0.350 \pm .004$	$+7.29$			
2880	$+0.379 \pm .005$	$+7.89$			

Average $k = 3.13 \pm 0.04 \times 10^{-4} \text{ sec}^{-1}$.

* $\text{Log}(a-x) = \text{log}([\alpha]_{D,\infty}^{25} - [\alpha]_{D,\text{obs.}}^{25})$

$\text{Log } a/(a-x) = \text{log}([\alpha]_{D,\infty}^{25} - [\alpha]_{D,0}^{25}) / ([\alpha]_{D,\infty}^{25} - [\alpha]_{D,\text{obs.}}^{25})$

dissolved in one ml. of bromoform and its infrared spectrum in the region 11.0-12.5 microns recorded. A plot of concentration versus absorbance showed good linearity as illustrated in Fig. 2.

By using the infrared kinetic method a number of kinetic runs on α,γ -dimethylallyl 2,6-dimethylbenzenesulfinate under various conditions at 70.07°, were carried out. The results obtained are summarized in Table V and an example of the calculations of the rate constants, taken from Run 14, is shown in Table VI.

The curve obtained by plotting the logarithm of the observed absorbance ($A_{\text{obs.}}$) versus time (Fig. 3) again indicated the presence of two diastereomers, previously detected with the active same sulfinate ester. In this case of racemic ester, two pairs of diastereomers were present i.e., (+)(+) - (+)(-) and (-)(-) - (-)(+). However, since (+)(+) and (-)(-) are optical enantiomers they reacted at the same rate. The same is true for the other racemate: (+)(-) and (-)(+). As a result, there would be only two different species with regard to rate of reaction.

The rate constants for the rearrangement of slow and fast reacting diastereomers were calculated in the following manner. The $A(\log I_0/I)$ values corresponding to each diastereomer were determined with the aid of the plot of $\log A_{\text{obs.}}$ versus time (Fig. 3), assuming the absorbance coefficients (ϵ) of the two diastereomers to be identical. The $A_{\text{obs.}}$ values related to the points lying on the straight line portion of the plot were assigned to the slow diastereomer. The $A_{\text{obs.}}$ corresponding to the first point on this line served as the "zero" time absorbance for the calculation of the rate constant of the slow diastereomer. To obtain the A values of the fast reacting

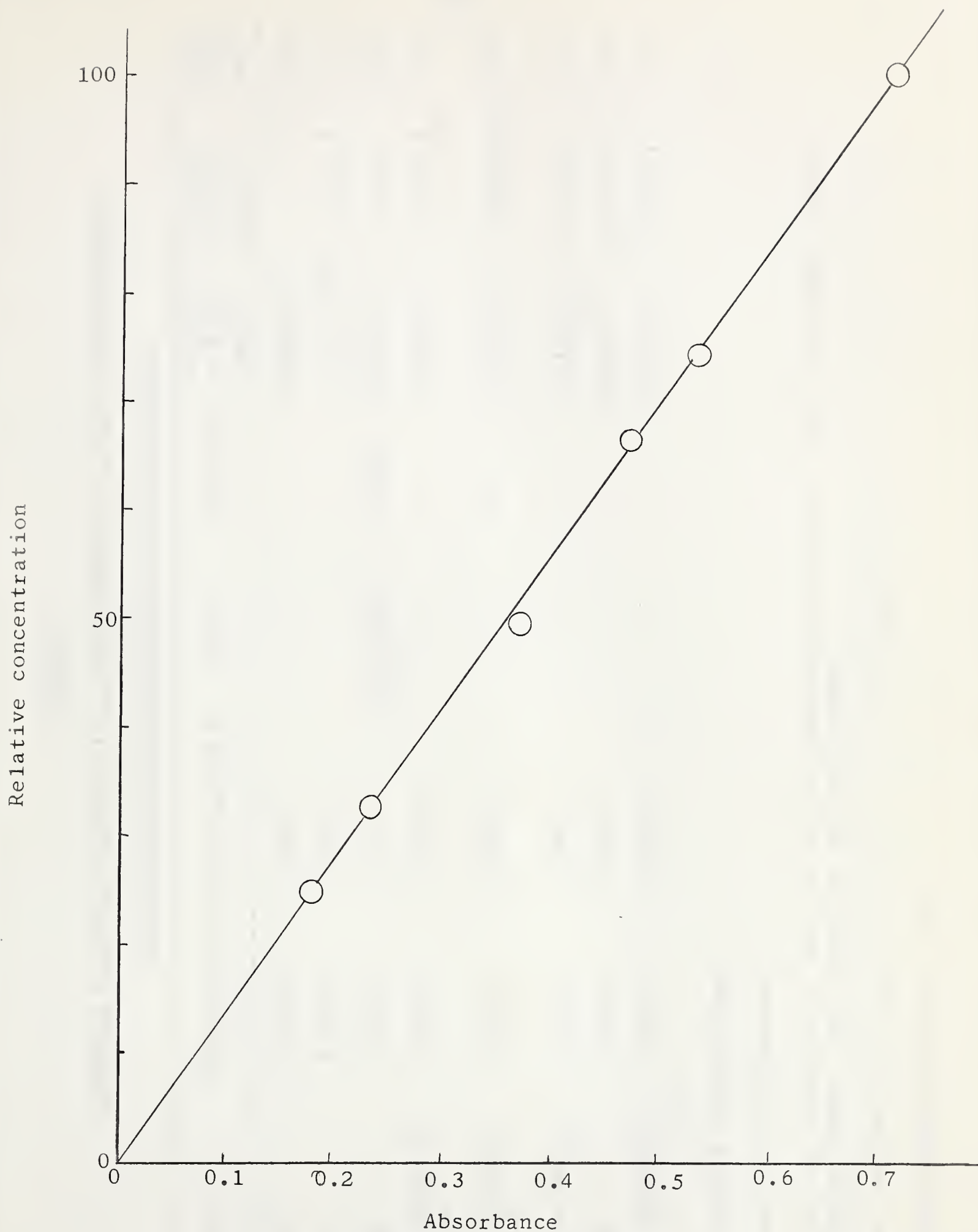


Fig. 2. Lambert-Beer law and extraction procedure control for α, γ -dimethylallyl 2,6-dimethylbenzenesulfinate (Band at 11.85μ measured; $100 \equiv 0.0259 \text{ M}$).

TABLE V

A summary of rate constants for rearrangement of α, δ -dimethylallyl2,6-dimethylbenzenesulfinate at $70.07 \pm 0.02^\circ$

Run #	Solvent	(Ester), M	(2,6-Lutidine), M	Salt	(Salt), M	S.R.D. ^a k x 10 ⁴ sec	F.R.D. ^b k x 10 ⁴ sec	Note- book ^c ref.
9	EtOH ^d	0.0195	0.0467	-	-	2.13+0.06	-	70-1
10	EtOH	0.0227	0.0472	-	-	2.38+0.239	13.4+1.5	74-1
16	EtOH	0.0230	0.0472	C ₈ H ₉ SO ₂ H ^e	0.0235	2.45+0.05	14.4+1.8	88-1
12	80% Dioxane -H ₂ O	0.0227	0.0490	-	-	3.88+0.22	15.3+1.1	77-1
13	90% Dioxane -H ₂ O	0.0227	0.0490	-	-	1.65+0.22	6.59+0.42	80-1
14	90% EtOH-H ₂ O	0.0228	0.0495	-	-	5.71+0.25	23.6+1.4	81-1
15	AcOH	0.0228	0.0495	-	-	14.8+1.7	42.4+11.9	86-1
16	60% EtOH-H ₂ O	0.0206	0.0495	-	-	26.5+1.6	65.4+11.6	93-1

a - Slow reacting diastereomer.

b - Fast reacting diastereomer.

c - Indicates the location of the run in the laboratory notebook. The first number refers to the page number, the second to the book number.

d - In this run slow reacting diastereomer was used (page 34).

e - 2.6-Dimethylbenzenesulfonic acid.

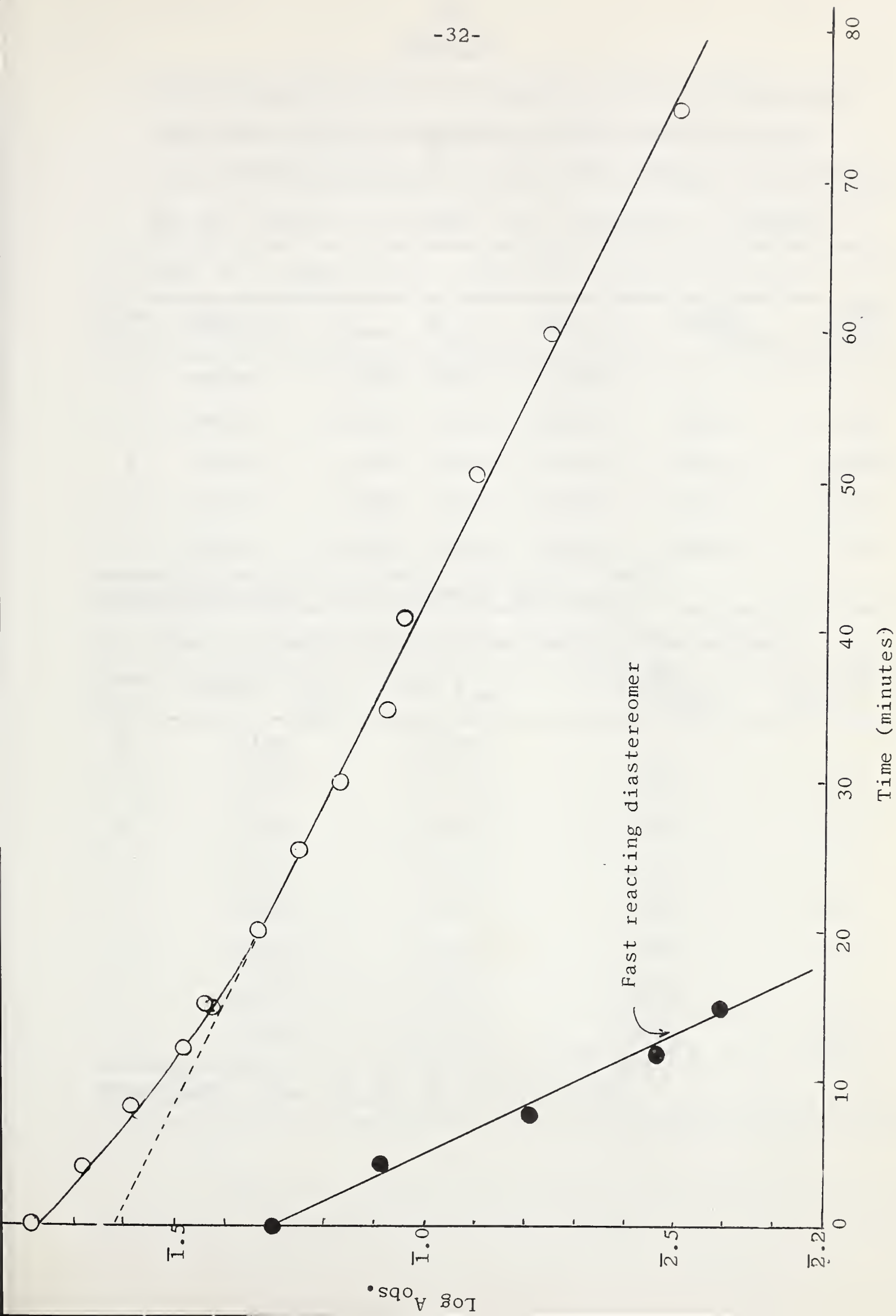


Fig. 3 - Plot of logarithm of absorbance of ester vs. time for the rearrangement of α, δ -dimethylallyl 2,6-dimethylbenzenesulfonate in 90.00% EtOH at 70.07° (Table IV).

TABLE VI

Calculations for the determination of the infrared rate constants in the rearrangement of α,δ -dimethylallyl

2,6-dimethylbenzenesulfinate in 90% EtOH-H₂O at 70.07 \pm 0.02°

Run #14 (Ester) = 0.0228M; (2.6-lutidine) = 0.0495M.

A. Rate of disappearance of Fast Reacting Diastereomer:

Time, min.	$\text{Log} \frac{I_0}{I} = A_{\text{obs.}}$	$A_{\text{ext.}}$	$A_{\text{calc.}}$	$\text{Log} A_{\text{calc.}}$	$\text{Log} \left(\frac{A_0}{A} \right)_{\text{calc.}}$	$k \times 10^3$ sec^{-1}
0	.6208	.4201	.2007	$\bar{1}.3025$	-	-
4	.4880	.3673	.1207	$\bar{1}.0816$.2209	2.12
8	.3807	.3211	.0596	$\bar{2}.7752$.5273	2.53
12	.3141	.2802	.0339	$\bar{2}.5302$.7723	2.47
15	.2783	.2535	.0248	$\bar{2}.3945$.9080	2.43

Average value of $k = 2.36 \pm 0.14 \times 10^{-3} \text{ sec}^{-1}$

Graphically (Fig. 3) $k = 2.39 \times 10^{-3} \text{ sec}^{-1}$

B. Rate of disappearance of Slow Reacting Diastereomer:

Time, min.	$\text{Log} \frac{I_0}{I} = A_{\text{obs.}}$	$\text{Log} A_{\text{obs.}}$	$\text{Log} \left(\frac{A_0}{A} \right)_{\text{obs.}}$	$k \times 10^4$ sec^{-1}
20	.2162	$\bar{1}.3349$	-	-
25	.1804	$\bar{1}.2562$.0787	6.04
30	.1549	$\bar{1}.1900$.1449	5.50
35	.1287	$\bar{1}.1096$.2253	5.77
40	.1028	$\bar{1}.0119$.3230	6.20
50	.0824	$\bar{2}.9159$.4190	5.35
60	.0589	$\bar{2}.7701$.5648	5.41
75	.0335	$\bar{2}.5250$.8099	5.65

Average value of $k = 5.71 \pm 0.25 \times 10^{-4} \text{ sec}^{-1}$

Graphically (Fig. 3), $k = 5.59 \times 10^{-4} \text{ sec}^{-1}$

diastereomer, the straight line portion of the plot was extrapolated to zero time. The antilogarithms of the extrapolated log A values afforded $A_{\text{ext.}}$, which represented the contribution of the slow diastereomer to the total absorbance. The differences between $A_{\text{obs.}}$ and $A_{\text{ext.}}$ afforded the A values for the fast reacting diastereomer ($A_{\text{calc.}}$). A plot of log $A_{\text{calc.}}$ versus time from the data obtained yielded a straight line (Fig. 3). The rate constants of both slow and fast diastereomers were calculated from the first-order kinetic expression, $k = 2.303/t \log A_0/A$.

In Run 9, a solution of α,γ -dimethylallyl 2,6-dimethylbenzenesulfinate (0.0504M) in anhydrous ethanol, with added 2,6-lutidine (0.0501M), was heated for 30 minutes at 70.07°. After extraction with ether and evaporation of the solvent, the sulfone was crystallized from pentane and separated by filtration. The unreacted sulfinate ester, recovered by evaporation of the pentane and consisting mainly of the slow reacting diastereomer, was then used for the determination of the rate constant listed in Table V (Run 9). The rate constant for the rearrangement of the slow diastereomer as obtained by using the practically pure diastereomer ($k = 2.13 \pm 0.06 \times 10^{-4} \text{ sec}^{-1}$, Run 9) is within experimental error to that obtained by using the mixture of both diastereomers ($k = 2.38 \pm 0.239 \times 10^{-4} \text{ sec}^{-1}$, Run 10). This fact indicates that the assumption which has been made with regard to the identity of the absorbance coefficients (ϵ) for the two diastereomers is correct, at least within experimental error.

Run 16 was carried out as a test of common ion rate depression. In acetic acid and 60% ethanol-water, the accuracy

of the rate constants was lower than the average because the rearrangement in these solvents was very fast, having a half-life of 4-6 minutes at 70.07°.

Two less quantitative kinetic experiments were performed. In one experiment, a cyclohexane solution of the sulfinate ester (0.0211M) over sodium carbonate was refluxed (78°), and portions of it removed at various time intervals. After evaporation of the solvent under reduced pressure, the infrared spectra of the residues were recorded. The reaction was 85% completed after 24 hours of refluxing ($k = \text{ca. } 2 \times 10^{-5} \text{ sec}^{-1}$). In the second experiment, a solution of the ester (0.0215M) in anhydrous ethanol with added sodium acetate (0.0610M) was refluxed (78°) for shorter periods of time. Portions of the solution were removed and extracted with ether. After washing the ether solutions with water and drying over magnesium sulfate, the ether was evaporated at the water pump and the infrared spectra of the residues recorded. The reaction was 90% completed after one hour of refluxing ($k = \text{ca. } 7 \times 10^{-4} \text{ sec}^{-1}$). In both cases sulfone was formed.

These results which were later used as a guide with respect to reaction time for the kinetic runs, also indicated that the rearrangement in ethanol was roughly 35 times faster than in cyclohexane.

DISCUSSION

Examination of the foregoing data gives an indication of the reactivity of α,γ -dimethylallyl 2,6-dimethylbenzenesulfinate. This ester was found to undergo rearrangement to α,δ -dimethylallyl 2,6-dimethylphenyl sulfone in various hydroxylic solvents (Table II), as well as in n-octane and cyclohexane. The sulfone was readily isolated in each case, in greater than 70% yield. No solvolysis products were isolated from the reaction of the sulfinate ester in buffered anhydrous ethanol and aqueous dioxane. From the reaction of the sulfinate ester in buffered acetic acid and 80% ethanol-water, only traces of acetate and alcohol, respectively, could be detected by infrared spectroscopy. However, since these solutions were heated for much longer periods than 10 half-lives, it is not known whether the observed solvolysis products represent solvolysis of the ester or a side reaction taking place during the extended heating. At the same time it should be emphasized, that solvolysis products such as α,δ -dimethylallyl alcohol, acetate and ether might have been lost during the work-up procedure, if formed in small quantities. Therefore, a definite decision with regard to the formation of solvolysis products from the reaction of α,δ -dimethylallyl 2,6-dimethylbenzenesulfinate cannot be made on the basis of these results alone.

In general, if the solvolysis of a sulfinate ester proceeds with carbon-oxygen bond fission, acid is produced. If an aqueous solvent is used, sulfur-oxygen bond fission will also produce acid. The acid produced in 10 half-lives sets an upper limit for the amount of solvolysis in any particular run.

Inspection of Table III shows that in anhydrous ethanol as solvent, no acid is produced in 10 half-lives. Accordingly, no solvolysis of the sulfinate ester occurred in this solvent. The reaction of the sulfinate ester in 60% ethanol-water in the presence of sodium acetate at 90.00° gave rise to 4.7% acid after 10 half-lives, while in the presence of 2,6 -lutidine at $70.07 \pm 0.02^\circ$, only 1.3% acid was produced in 10 half-lives. Because of the low yield of acid, it is difficult to decide whether it should be attributed to solvolysis by sulfur-oxygen or by carbon-oxygen bond fission.

In anhydrous ethanol, the occurrence of any sulfur-oxygen bond fission during the reaction of α, γ -dimethylallyl 2,6 -dimethylbenzenesulfinate, should result in the formation of ethyl 2,6 -dimethylbenzenesulfinate. The failure to detect this compound in the reaction products, would tend to eliminate the operation of sulfur-oxygen bond fission in ethanol under the conditions employed.

The results of the kinetic investigation and the results obtained from the reaction of the optically active α, γ -dimethylallyl 2,6-dimethylbenzenesulfinate, provide some information with regard to the mechanism of rearrangement of sulfinate to sulfone. Inspection of Table V, shows that the rearrangement of the sulfinate ester is accelerated by the increase in solvent ionizing power. The relative rates of rearrangement in various solvents are presented in Table VII.

The observed relation between rate of rearrangement and solvent ionizing power is indicative of a polar transition state. However, the magnitude of the solvent effect is considerably

TABLE VII

Relative rates of rearrangements of α,γ -dimethylallyl
2,6 -dimethylbenzenesulfinate in various solvents at
70.07 \pm 0.02°.

Solvent	Relative rate	
	S.R.D. ^a	F.R.D. ^b
Cyclohexane	ca. 0.04 ^c	-
90% Dioxane-water	1.00	1.00
Ethanol	1.44	2.03
80% Dioxane-water	2.35	2.32
90% Ethanol-water	3.46	3.58
Acetic acid	8.97	6.43
60% Ethanol-water	16.06	9.93

a - Slow reacting diastereomer.

b - Fast reacting diastereomer.

c - This value is based on the relative rate between ethanol and cyclohexane (ca.35) at 78°.

smaller than that observed with ionizing systems. For example, Darwish and McLaren(27) have found that the rate of solvolysis and rearrangement of benzhydryl 2,6 -dimethylbenzenesulfinate in ethanol is 26.1 times faster than in 90% dioxane-water. The same change in solvent, increases the rate of rearrangement of α,γ -dimethylallyl 2,6 -dimethylbenzenesulfinate by a factor between 1.4 and 2. Similarly, Smith, Fainberg and Winstein(18) have found that the rate of solvolysis of p-methoxyneophyl p-toluenepulfonate in ethanol is larger than in diethyl ether

($D = 4.23$) by a factor of ca. 10^4 . The rate of rearrangement of α,δ -dimethylallyl 2,6-dimethylbenzenesulfinate in ethanol, is only ca. 35 times faster than in cyclohexane ($D = 2.02$). These results tend to suggest that the change in charge separation between the ground state and transition state, for the rearrangement of α,δ -dimethylallyl 2,6-dimethylbenzenesulfinate, is much smaller than in the solvolysis of benzhydryl 2,6-dimethylbenzenesulfinate or *p*-methoxyneophyl *p*-toluenesulfonate.

The formation of optically active α,δ -dimethylallyl 2,6-dimethylphenyl sulfone from the reaction of the corresponding optically active sulfinate ester, tends to eliminate an ionic mechanism involving dissociated ions as the only reaction path for rearrangement. Such a mechanism would be expected to yield racemic product, since the free carbonium ion would be optically inactive. The retention of optical activity is consistent with either an ion-pair mechanism or a cyclic intramolecular rearrangement.

It is not known whether or not the retention of optical activity accompanying the rearrangement of the active sulfinate to sulfone is complete. Similarly it is not possible to determine from the available data the relationship between the configuration of the active sulfone and that of starting material. These points are treated in Chapter 2.

The rate of rearrangement of α,δ -dimethylallyl 2,6-dimethylbenzenesulfinate in buffered anhydrous ethanol was not affected significantly by the addition of 2,6-dimethylbenzenesulfinate anion (Table V). However, the result of this

common ion rate depression test does not provide unequivocal evidence for the exclusion of a dissociated ion mechanism, since it is not known whether the return of such ions would regenerate sulfinate ester or yield sulfone exclusively.

It is interesting to point out the relatively high degree of reactivity of α,δ -dimethylallyl 2,6-dimethylbenzenesulfinate, as deduced from the following considerations. The rate of solvolysis of benzhydryl 2,6-dimethylbenzenesulfinate (27) in ethanol at 90° ($k = 2.38 \times 10^{-5} \text{ sec}^{-1}$), is of the same order of magnitude as that of benzhydryl chloride(33) in the same solvent at 25° ($k = 5.75 \times 10^{-5} \text{ sec}^{-1}$). On the other hand, the rate of rearrangement of α,δ -dimethylallyl 2,6-dimethylbenzenesulfinate in ethanol at 70° ($k = 1.34 \times 10^{-3}$, fast diastereomer), is 20 times faster than the rate of solvolysis of α,δ -dimethylallyl chloride (p.786 of ref. 1) in the same solvent, at 25° ($k = 6.6 \times 10^{-5} \text{ sec}^{-1}$). If the difference in rate between 70° and 90° is taken in account (a factor of ca.5), it results that the rate of α,δ -dimethylallyl 2,6-dimethylbenzenesulfinate is faster than that of the corresponding chloride by two powers of ten.

The evidence presented in this chapter is indicative of a cyclic intramolecular mechanism for the rearrangement of α,δ -dimethylallyl 2,6-dimethylbenzenesulfinate to the corresponding sulfone. A more detailed discussion of this mechanism is deferred to subsequent chapters.

EXPERIMENTAL

All melting and boiling points are uncorrected. Melting points were taken on a Hershberg melting point apparatus, using a set of Anschutz thermometers.

Refractive indices were taken on a Bausch and Lomb Abbe-3L Refractometer which was thermostated at 25°.

The infrared spectra were recorded on Perkin Elmer Recording Infrared Spectrophotometers, Model 21 and Model 221G, using sodium chloride sealed cells. The former was used for kinetic measurements and the latter for identification.

The n.m.r. spectra were recorded on a Varian Analytical Spectrophotometer, Model A-60.

Solvents

Ethanol

Anhydrous ethanol was prepared from 98% ethanol according to the method of Lund and Bjerrum as described by Fieser(34). This method is based on the reaction between magnesium ethoxide and water, to yield the insoluble magnesium hydroxide. Since the ethanol employed was contaminated with some benzene, the first few hundred ml. of each liter of distillate were discarded. The dryness of this and other purified solvents was checked by Karl Fischer titrations, as described by Winstein and co-workers(18). The purified ethanol contained no more than 0.002% water.

Dioxane

Eastman Organic "white label" grade dioxane was purified according to the method suggested by Fieser(35). The purified dioxane (b.p.97-98°) contained less than 0.001% water, as determined by a Karl Fischer titration.

Acetic acid

Canadian Industries Ltd. glacial acetic acid (99.8%) was purified by a procedure described by Fainberg and Winstein (36). The solvent was first treated with acetic anhydride in equivalent amount to that of the water present, as determined by a Karl Fischer titration, and subsequently refluxed for 12 hours and fractionally distilled. The water content of the distillate was determined by Karl Fischer titration, and enough acetic anhydride was added to neutralize the water present and make up a 0.1M solution in acetic anhydride. The 0.1M solution of acetic anhydride in acetic acid thus obtained, was refluxed for another 12 hours.

Cyclohexane

Fisher certified reagent grade cyclohexane was purified by shaking mechanically a mixture of this material with portions of concentrated sulfuric acid, until no darkening of the acid was observed. The cyclohexane was then separated from the acid by means of a separatory funnel, washed with water several times, and dried over anhydrous sodium carbonate. This was followed by fractional distillation through an 18" Vigreux column, the fraction boiling at 77-78° being collected.

Pentane

Phillips Petroleum 66 technical grade pentane was purified by refluxing overnight with, and distillation from, phosphorous pentoxide.

Diethyl ether

Mallinckrodt AR anhydrous ether was used without further purification.

Mixed solvents

X% Ethanol-water means a solution prepared by mixing x volumes of ethanol with 100 - x volumes of boiled distilled water at 25°. The same pipette was used for measuring all volumes. Other mixed solvents were made up in the same manner.

Reagents and Materials

Sodium acetate

Merck reagent grade anhydrous sodium acetate was used without further purification.

2,6-Lutidine

Eastman Organic practical grade 2,6-lutidine was purified by refluxing with, and distillation from, barium oxide. It was stored in a dark, screw-capped bottle over potassium hydroxide pellets.

α,δ -Dimethylallyl alcohol

A 48.6 g. quantity (2.0 moles) of magnesium turnings was placed in a three liter three-necked flask, equipped with a stirrer, a condenser, and an additional funnel. A 284 g. quantity (2.0 moles) of iodomethane, dissolved in one liter of anhydrous ether, was added gradually with stirring and cooling in an ice-water bath. After the addition of the ether solution had been completed, the cooling bath was removed and reaction mixture gently refluxed on a steam bath for one hour. The solution of the Grignard reagent was then cooled in an ice-water bath, and freshly distilled crotonaldehyde, b.p. 97-99.5° (140 g., 2.0 moles), dissolved in 300 ml. of ether, was added slowly with stirring. This was followed by the addition of the equivalent amount (300 ml.) of saturated ammonium chloride

solution in a dropwise manner with continuous stirring and cooling. The appearance of a white precipitate was observed. The ether layer was decanted into a large Erlenmyer flask. The precipitate was washed several times with ether and washings combined with the original ether solution. After drying over anhydrous magnesium sulfate, the ether was evaporated at the water pump and residue distilled under reduced pressure. The alcohol was collected at 6 mm. and room temperature. The receiver was cooled in a dry ice-acetone bath during the distillation of the alcohol to avoid loss of material. Yield, 105 g. (61%), n_D^{25} 1.4260 (reported(32) yield, 63%, n_D^{25} 1.4260).

2,6-Dimethylbenzenesulfonic acid

A 30 g. quantity (0.25 mole) of 2,6-dimethylaniline was dissolved in a cold mixture of 600 ml. water and 150 ml. concentrated sulfuric acid in a two liter Erlenmeyer flask, equipped with a stirrer and a dropping funnel. The solution was cooled to 0°, using an ice-salt bath. 2,6-Dimethylanilinium sulfate crystallized from the solution. An 18 g. quantity (0.26 mole) of sodium nitrite, dissolved in 100 ml. of water, was added in a dropwise manner with stirring. When the addition was completed, all the solid had disappeared. A previously cooled mixture of 80 ml. concentrated sulfuric acid and 60 ml. water was added to the clear reaction solution. The stirring was stopped, and sulfur dioxide was bubbled in for one hour. Copper powder (200 g.) was then added gradually over a period of one hour with stirring, the temperature being maintained at 0°. The addition of sulfur dioxide and stirring were continued overnight, while the mixture was allowed to warm up to room

temperature. The reaction mixture was filtered with suction and filtrate discarded. The copper mash was added gradually to one liter of 10% sodium carbonate solution. The copper was separated by filtration with suction, and filtrate acidified with cold 50% by volume sulfuric acid solution, until no more precipitation of the 2,6 -dimethylbenzenesulfinic acid occurred. The 2,6 -dimethylbenzenesulfinic acid was filtered with suction, dried in a desicator over Drierite under vacuum, and stored in the freezer before use. Yield, 27 g. (64%), m.p. 92-94° (decomposition), (reported (p. 70 of Ref. 24) m.p. 95.0-98.0°).

2,6 -Dimethylbenzenesulfinyl chloride.

2,6 -Dimethylbenzenesulfinic acid (13 g., 0.08 mole) was placed in a 300 ml. round bottom flask. After the addition of 40 ml. of pentane, the flask was fitted with a condenser at the top of which a pressure equalizing dropping funnel was attached, protected with a drying tube. A 23 g. quantity (0.19 mole) of thionyl chloride dissolved in 20 ml. of pentane was added in a dropwise manner over a period of one hour, at room temperature. The reaction was allowed to proceed until the evolution of gas subsided and all solid disappeared. When the reaction was completed, the tarry residue was filtered off by suction, using a sintered glass funnel. The pentane and excess thionyl chloride were removed by pumping under vacuum overnight to yield a hygroscopic brown oil. Yield, 11 g. (70%).

α,γ -Dimethylallyl 2,6 -Dimethylbenzenesulfinate

A 4.6 g. quantity (0.023 mole) of 2,6 -dimethylbenzenesulfinyl chloride was weighed into a 250 ml. round bottom flask, to which was added 30 ml. of Karl Fischer reagent grade pyridine.

The flask was provided with a drying tube and immersed in a dry ice-acetone bath. A previously cooled solution of 2.0 g. (0.023 mole) of α,γ -dimethylallyl alcohol in 10 ml. of pyridine was added in small portions with shaking. The reaction mixture with the cooling bath were transferred to the refrigerator and left there overnight. The contents of the flask were poured over a mixture of ice and 50 ml. of concentrated hydrochloric acid. The mixture was extracted with 300 ml. of ether. The ether layer was washed successively with three 100 ml. portions of water, 10% sodium carbonate solution until no yellow colour appeared in the aqueous layer, and then with water until washings were neutral to litmus. After drying over anhydrous magnesium sulfate and evaporation of the ether using a water pump, the sulfinic ester was obtained as a yellowish oil. The ester was stored in the refrigerator, in pentane solution over anhydrous potassium carbonate. Yield, 3.6 g. (60%), n_D^{25} 1.5353, infrared (CS_2): 730, 770, 840, 890, 960, 1025, 1125(s) cm^{-1} . The n.m.r. data are listed in Table XI.

Procedure for product analysis.

In a typical procedure, a 1.110 g. quantity (0.00466 mole) of α,γ -dimethylallyl 2,6-dimethylbenzenesulfinate and a 3.000 g. quantity (0.00832 mole) of $\text{Bu}_4\text{NOAc} \cdot \text{HOAc}$ were weighed into a 200 ml. volumetric flask. 80% Dioxane-water solvent was added to the mark, and the solution shaken vigorously. The solution was transferred to a flask with a constricted neck, sealed and immersed in the $90.00 \pm 0.03^\circ$ constant temperature oil bath. After seven days, the flask was withdrawn from the bath and quenched by plunging in an ice-water bath. When the

flask was opened, 160 ml. of solution was removed with an automatic pipette and transferred to a two liter separatory funnel containing 800 ml. of ether. The ether solution was washed five times with 300 ml. portions of water, shaking the funnel 50 times for each washing, and then dried over anhydrous magnesium sulfate. On evaporation of the ether at the water pump at room temperature, 0.756 g. of material was obtained. When placed in the refrigerator the material crystallized. The infrared spectrum showed the presence of sulfone only. The sulfone was purified by recrystallization from pentane at 0°. Yield, 85.1%, m.p. 56.0-58.0°, infrared (CS_2): 725, 770(s), 960, 1010, 1115, 1145(s) and 1310(s) cm^{-1} . The n.m.r. data are listed in Table XI.

Analysis. Calculated for $\text{C}_{13}\text{H}_{18}\text{O}_2\text{S}$: C, 65.51; H, 7.61; S, 13.45. Found: C, 65.47, 65.60; H, 7.91, 7.70; S, 13.33.

Titrimetric measurements

The titrimetric run in 80% dioxane-water is described below as an example of the procedure employed for all solvents, except acetic acid.

A 0.542 g. quantity (0.00228 mole) of α, γ -dimethylallyl 2,6-dimethylbenzenesulfinate, and a 1.600 g. quantity (0.00443 mole) of $\text{Bu}_4\text{NOAc} \cdot \text{HOAc}$ were weighed into a 100 ml. volumetric flask. 80% Dioxane-water was added to the mark, and the solution was shaken vigorously. Portions of this solution were transferred to ampoules, such that they contained slightly over 5 ml. The ampoules were sealed, and immersed in the $90.00 \pm 0.03^\circ$ constant temperature oil bath at a recorded time. The ampoules were removed from the bath at the time

intervals indicated below, and placed into an ice-water bath to quench the reaction. After the ampoules had been allowed to equilibrate at room temperature, they were opened and 5 ml. aliquots removed, using a calibrated automatic pipette. The 5 ml. aliquot was delivered into 20 ml. of boiled distilled water, and titrated with a 0.0501 M solution of NaOMe in methanol to the pink end-point of phenolphthalein. The following results were obtained:

Time, hours:	0	2	12	14	26	48	99	143
Ml. of base:	4.75	4.80	4.91	5.05	5.00	5.27	5.14	5.20

The acid produced during the reaction of the sulfin-ate ester in acetic acid with sodium acetate present, was determined by titrating 5 ml. aliquots of solution with 0.0411 M HClO_4 in acetic acid, to a green end-point of naphtholbenzein (0.5% in acetic acid).

The resolution of α,γ -dimethylallyl alcohol (31,32).

(a) α,γ -Dimethylallyl acid phthalate.

In a one liter round bottom flask were placed 115 g. (1.34 mole) of α,γ -dimethylallyl alcohol, 198 g. (1.34 mole) of phthalic anhydride, and 120 g. (1.52 mole) of pyridine. The flask was then fitted with a condenser, and heated on the steam bath for one hour. The solution was allowed to cool to room temperature, and poured into a one liter beaker containing a mixture of ice and 125 ml. of concentrated hydrochloric acid. The product, which separated as an oil, was extracted with one liter of ether. The ether solution was washed with water, dilute hydrochloric acid solution and water. After drying over anhydrous magnesium sulfate, the ether was evapor-

ated at the water aspirator. The amorphous solid residue was crystallized from a mixture of "Skellysolve B" and methylene chloride. A 235 g. quantity, yield 75.1%, of the compound was obtained and melted at 78-84° (reported(32) yield 89%, m.p. 79-86°).

(b) (-)-Brucine salt of (+)- α,γ -dimethylallyl acid phthalate

A 200 g. quantity (0.854 mole) of α,γ -dimethylallyl acid phthalate was placed in a two liter Erlenmeyer flask, and dissolved in a mixture of 680 ml. of acetone and 340 ml. of chloroform. The solution was warmed on a steam bath, and 340 g. (0.862 mole) of brucine was added gradually. On cooling, the clear solution was placed in the refrigerator and left there overnight. The salt which crystallized from the solution was separated by filtration with suction, and recrystallized from acetone-chloroform (2:1) several times. Yield, 204 g. (75.6%), m.p. 166-168° (reported(32) yield 83%, m.p. 168.5-169.5°).

(c) (+)- α,γ -Dimethylallyl acid phthalate

A 204 g. quantity (0.325 mole) of (-)-brucine (+)- α,γ -dimethylallyl acid phthalate was treated with 400 ml. of cold 4N hydrochloric acid solution in a two liter beaker. The (+)- α,γ -dimethylallyl acid phthalate, which separated as a viscous oil, was extracted with one liter of ether. The aqueous layer was separated, and combined with the acidic washings of the ether layer. The ether layer was washed with water until washings were neutral to litmus, and dried over anhydrous magnesium sulfate. After removal of the ether using a water pump, the residue was crystallized from a mixture of "Skellysolve

B'' - methylene chloride. Yield, 50.5 g. (66.5%), m.p. 82-84° (reported(32) yield 75%, m.p. 82-85°). $[\alpha]_D^{25} +23.34^\circ$ ($\underline{1} = 1$, $\underline{c} = 5$, CHCl_3), reported(31) $[\alpha]_D +38.75^\circ$ ($\underline{c} = 10$, $\underline{1} = 2$, ether).
(d) (+)- α, δ -Dimethylallyl alcohol.

In a typical experiment, a 10 g. quantity (0.0427 mole) of (+)- α, δ -dimethylallyl acid phthalate was placed in a 100 ml. round bottom flask, and 22 ml. of 8N NaOH solution was added to it. A condenser was attached to the flask, and the mixture warmed on a steam bath for 20 minutes. On cooling, the alcohol which separated as an oil was extracted with 140 ml. of ether. The ether solution was washed with water, and after drying over anhydrous magnesium sulfate, the ether was removed by distillation through a Vigreux column. Yield, 2.6 g. (70.8%), $n_D^{25} 1.4250$, $[\alpha]_D^{25} -0.261 \pm .007^\circ$ ($\underline{1} = 1$, neat), reported(32) yield 83%, $[\alpha]_D -0.07 \pm .02^\circ$ ($\underline{1} = 1$, neat)).
(+)- α, δ -Dimethylallyl 2,6-dimethylbenzenesulfinate.

This ester was prepared by the method described for the preparation of the racemic sulfinate ester (p.45). Starting with 2.0 g. (0.024 mole) of (+)- α, δ -dimethylallyl alcohol and 4.6 g. (0.025 mole) of 2,6-dimethylbenzenesulfinyl chloride, a yield of 3.5 g. (58.3%) of the optically active sulfinate ester was obtained. $n_D^{25} 1.5423$, $[\alpha]_D^{25} +3.86^\circ$ ($\underline{1} = 1$, $\underline{c} = 5$ in ethanol); $[\alpha]_D^{25} +4.23^\circ$ ($\underline{1} = 4$, $\underline{c} = 2$ in CHCl_3).
Rearrangement of (+)- α, δ -dimethylallyl 2,6-dimethylbenzenesulfinate in ethanol.

(+)- α, δ -dimethylallyl 2,6-dimethylbenzenesulfinate (1.200 g., 0.00504 mole) and sodium acetate (0.412 g., 0.00503 mole) were weighted into a 100 ml. volumetric flask. Anhydrous ethanol was added to the mark and solution shaken vigorously.

A 50 ml. portion of this solution was transferred to another flask which was sealed and immersed in the $70.07 \pm 0.02^\circ$ constant temperature bath for 30 minutes. After quenching the reaction by cooling in an ice-water bath, the solution was transferred to a separatory funnel containing 250 ml. of ether and 100 ml. of water, and shaken 50 times. The aqueous layer was discarded and washing repeated four times in the same manner. After drying over anhydrous magnesium sulfate and evaporation of the ether at the water aspirator, the residue (0.433 g.) was dissolved in a few ml. of pentane and placed in the refrigerator for 36 hours. The material which crystallized out melted at $73-75^\circ$, $[\alpha]_D^{25} +6.44^\circ$ ($\underline{l} = 4$, $\underline{c} = 1.28$ in ethanol). The infrared spectrum in CS_2 was identical with that of rac. - α, δ -dimethylallyl 2,6 -dimethylphenyl sulfone.

The second 50 ml. portion of the original solution was heated in a sealed flask for 23 hours at $70.07 \pm 0.02^\circ$ in the constant temperature bath. After cooling, it was worked up as described above. The residue obtained (0.550 g.) was dissolved in a few ml. of pentane and placed in the refrigerator to allow for crystallization. The crystalline material which was separated had a m.p. of $73-75^\circ$ and $[\alpha]_D^{25} +7.05^\circ$ ($\underline{l} = 4$, $\underline{c} = 1$ in ethanol). The infrared (CS_2) was identical to that of the above sample.

Isolation of (-)- α, δ -dimethylallyl 2,6 -dimethylbenzenesulfinate.

(+)- α, δ -Dimethylallyl 2,6 -dimethylbenzenesulfinate (0.562 g., 0.00236 mole) and 2,6 -lutidine (0.278 g., 0.00260 mole) were weighed into a 50 ml. volumetric flask, and anhydrous

ethanol added to the mark. After mixing of the components, the solution was transferred to a flask with a constricted neck, the flask was sealed and immersed in the $70.07 \pm 0.02^\circ$ constant temperature oil bath for 30 minutes. After the reaction had been quenched, the flask was opened and its contents transferred to a separatory funnel, containing 250 ml. of ether. The ether solution was washed five times with 100 ml. portions of water, and dried over anhydrous magnesium sulfate. After filtration of the magnesium sulfate and evaporation of the ether at the water pump, the oily residue obtained (0.519 g.) was dissolved in 15 ml. of pentane and left in the refrigerator overnight. A portion of the material crystallized from the solution. The pentane solution was decanted to a 50 ml. pear shaped flask and cooled in a dry ice-acetone bath. More material crystallized from the solution. The pentane solution was decanted to another pear shaped flask. After evaporation of the pentane at the water pump, an oily residue (0.200 g.) was obtained.

$[\alpha]_D^{25} -24.30^\circ$ ($\underline{1} = 4$, $\underline{c} = 1.76$ in ethanol). The infrared spectrum in carbon disulfide was similar to that of the racemic sulfinate ester (p.46), showing some contamination with sulfone (1310 cm^{-1}).

Kinetic measurements.

Polarimetric method.

The appropriate quantities of (+)- α, δ -dimethylallyl 2,6 -dimethylbenzenesulfinate and sodium acetate or 2,6 -lutidine were weighed in a volumetric flask and anhydrous ethanol was added to the mark. The solutions contained 1.200 g. of ester per 100 ml. of solvent. After mixing, the solutions were trans-

ferred to ampoules in portions of ca. 7 ml., sealed and immersed in the $70.07 \pm 0.02^\circ$ constant temperature oil bath at a recorded time. At appropriate intervals ampoules were removed from the oil bath and transferred to an ice-water bath to quench the reaction. After the ampoules had been equilibrated at 25° and opened the solutions were transferred to a 4 dm. polarimetric tube, and optical rotations measured on a Model 80 Rudolph Polarimeter, using a sodium lamp as the light source.

Infrared method.

The buffered solution of α, β -dimethylallyl 2,6-dimethylbenzenesulfinate, prepared by weighing out the components in a volumetric flask and addition of the appropriate solvent up to the mark, was distributed into ampoules so that they contained slightly over 5 ml. of solution. The ampoules were sealed and immersed in the $70.07 \pm 0.02^\circ$ constant temperature oil bath at a recorded time. At appropriate time intervals, the ampoules were transferred to an ice-water bath to quench the reaction. After equilibration at 25° , the ampoule was opened and a 5 ml. aliquot was removed using a calibrated automatic pipette and delivered into a 60 ml. separatory funnel, containing 25 ml. of pentane and 10 ml. of distilled water. After shaking the stoppered funnel 50 times, the water layer was discarded, and washing with water was repeated in a similar manner four times. After drying over anhydrous sodium carbonate for one hour, filtration of the drying agent and subsequent evaporation of the pentane at the water aspirator the residue (contained in a 50 ml. pear shaped flask) was diluted with 1 ml. of Eastman spectro grade bromoform

by means of an automatic pipette. This solution was transferred to a 0.5 mm. sodium chloride cell, previously balanced with a reference cell of the variable type, and the infrared spectrum recorded on a Model 21 Perkin Elmer Infrared Spectrophotometer, using a 20 cm. per micron scale setting. The region of 11.0 to 12.5 microns was scanned at room temperature to determine the absorbance of the sulfinate band at 11.85 microns.

Lambert-Beer law and extraction procedure control.

A standard solution of α,δ -dimethylallyl 2,6-dimethylbenzenesulfinate (0.0259 M) in anhydrous ethanol was prepared in the usual manner. Solutions of lower concentrations were then prepared, by diluting aliquots of this solution with anhydrous ethanol using the same automatic pipette throughout. Aliquots of 5 ml. from each solution of known concentration, including the original one, were extracted, diluted with 1 ml. of bromoform, and the absorbance of the solution recorded on the infrared spectrophotometer in exactly the same manner as described in the preceding section (infrared method). The results obtained afforded the plot of absorbance ($\log I_0/I$) versus concentration illustrated in Fig. 2.

CHAPTER 2

Allylic Isomerization, Substituent Effects and Activation Enthalpies and Entropies for the Rearrangement of Allylic 2,6-Dimethylbenzenesulfonates to Sulfones.

In order to obtain further information about the mechanism of rearrangement of α, β -dimethylallyl 2,6-dimethylbenzenesulfonate which was described in the previous chapter, it was considered desirable to investigate the occurrence and extent of allylic rearrangement accompanying the sulfonate to sulfone rearrangement, as well as the effect of substituents on the rate of this reaction. For this purpose five more compounds, namely, allyl, crotyl (β -methylallyl), α -methylallyl, cinnamyl (β -phenylallyl), and α -phenylallyl 2,6-dimethylbenzenesulfonates were selected. With the exception of the allyl ester, these compounds were potentially suited for the study of allylic rearrangement. To establish whether allylic rearrangement had occurred in the rearrangement of α, β -dimethylallyl 2,6-dimethylbenzenesulfonate, the relation between the configuration of the active sulfone and active sulfonate, from which it was obtained was determined. A kinetic study of the rearrangement of the above mentioned allylic sulfonates, including the available data for α, β -dimethylallyl ester, would enable one to determine the effect of a methyl or phenyl group in one or both allyl positions on the reaction rate. The activation entropy and enthalpy of the rearrangement reactions were also determined.

RESULTS

- A. The syntheses and reactions of allyl, crotyl, α -methylallyl, cinnamyl and α -phenylallyl 2,6-dimethylbenzenesulfonates.

Crotyl alcohol was obtained by the reduction of crotonaldehyde with lithium aluminum hydride. α -Methylallyl and α -phenylallyl alcohols were prepared by treatment of acrolein with methylmagnesium iodide and phenylmagnesium bromide, respectively. Commercially available allyl and cinnamyl alcohols were used. The 2,6-dimethylbenzenesulfonate esters of these alcohols were prepared by treatment of the appropriate alcohol with 2,6-dimethylbenzenesulfonyl chloride in pyridine in a dry ice-acetone bath. Some physical properties of the various allylic alcohols, 2,6-dimethylbenzenesulfonates and 2,6-dimethylphenyl sulfones are shown in Table VIII. Cinnamyl 2,6-dimethylbenzenesulfonate was the only ester which was obtained in a crystalline form. It was easily crystallized from pentane. As indicated in Table VIII, all esters show strong infrared absorption at $1130-1140\text{ cm}^{-1}$, which is a characteristic region for sulfonate esters(30). Crotyl and cinnamyl 2,6-dimethylbenzenesulfonates, and their parent alcohols, gave rise to intense infrared bands at $960-963\text{ cm}^{-1}$ (CS_2). On this basis these compounds were assigned a trans configuration at the olefinic double bond(29).

In order to establish the type of reaction that these esters would undergo under solvolytic conditions, they were allowed to react in one or more hydroxylic solvents. Buffered solutions were used in all cases to avoid catalysis by strong

TABLE VIII

Physical properties of various allylic alcohols, 2,6-dimethylbenzene-sulfonates and 2,6-dimethylphenyl sulfones.^a

	Alcohol		Ester ^b		Sulfone ^c	
	n_D^{25}	IR abs. ^d cm ⁻¹	n_D^{25}	IR abs. ^d cm ⁻¹	M.p., °C	IR abs. ^d cm ⁻¹
Allyl	1.4113	3605	1.5480	1140, 970	42.4-43.2	1320, 1150
Crotyl	1.4238	3610	1.5442	1135, 900	1.5466 ^f	1320, 1150
α-Methylallyl	1.4090	3600	1.5370	1140, 835	59.0-60.2	1315, 1150
Cinnamyl	1.5810	3600	39.8-41.0 ^e	1135, 830	140.5-140.8	1320, 1150
α-Phenylallyl	1.5401	3600	1.5795	1140, 925	130.8-131.4	1315, 1145

a - The n.m.r. data are reported in Table XI.

b - 2,6-Dimethylbenzenesulfinate.

c - 2,6-Dimethylphenyl sulfone.

d - In carbon disulfide.

e - Melting point, °C.

f - Refractive index, n_D^{25} .

acid. The results obtained are reported in Table IX.

The experimental procedure for carrying out these reactions and isolation of products was similar to that used with α,δ -dimethylallyl 2,6-dimethylbenzenesulfinate (Chapter 1). The sulfone formed from the rearrangement of α -phenylallyl 2,6-dimethylbenzenesulfinate in 60% ethanol-water at 25° gradually crystallized from the solution. Similarly, the sulfone formed from the rearrangement of cinnamyl 2,6-dimethylbenzenesulfinate in 60% ethanol-water at 90°, crystallized in fine needles, after cooling the solution at the end of the reaction. In these cases most of the sulfone was recovered by simple filtration of the reaction solution. The filtrates were then subjected to the usual extraction procedure and product identification.

As these product analyses were preceded by kinetic measurements in the same solvents, the reaction times were chosen to correspond roughly to 10 half-lives for the reaction. With the exception of crotyl 2,6-dimethylphenyl sulfone, obtained from the rearrangement of α -methylallyl 2,6-dimethylbenzenesulfinate, all sulfones could be crystallized from pentane or pentane-ether.

The identification of the various sulfones was based on infrared and n.m.r. spectra, C,H,S analysis and melting point wherever appropriate. The infrared and n.m.r. data proved very useful in the determination of the nature of the allylic isomer. The infrared absorption of the double bond in the region 900-1000 cm^{-1} was used for this purpose. The data are summarized in Table X, together with the pertinent data of the corresponding alcohols and sulfinate esters.

TABLE IX

A summary of reaction conditions and products for the rearrangement of various allylic 2,6-dimethylbenzenesulfonates to corresponding sulfones

2,6-Dimethylbenzene-sulfinate	Solvent	Time, hrs.	Temp., °C.	(Ester), M	(Base), M	Yield, %	Sulfone Identity
Allyl	60% EtOH-H ₂ O	379	90	0.0438	0.0839 ^a	78.2	Allyl
Crotyl	AcOH	42	80	0.0253	0.0518 ^a	91.5	α-Methylallyl
"	60% EtOH-H ₂ O	16	90	0.0369	0.0837 ^a	85.2	- " -
α-Methylallyl	AcOH	4	90	0.0406	0.1024 ^b	86.2	Crotyl
"	60% EtOH-H ₂ O	2	90	0.0409	0.0858 ^a	72.7	- " -
Cinnamyl	AcOH	4	90	0.0200	0.0534 ^b	86.2	α-phenylallyl
"	60% EtOH-H ₂ O	2	90	0.0174	0.0458 ^a	89.0	- " - ^c
α-phenylallyl	60% EtOH-H ₂ O	20	25	0.0325	0.0729 ^b	87.0	Cinnamyl

a - 2,6-Lutidine.

b - Sodium acetate.

c - The sulfone in this case was contaminated with app. 7% of the other allylic isomer.

TABLE X

The olefinic infrared absorption of some allylic compounds in the region 900 - 1000 cm^{-1} (CS_2).

	Alcohol	Ester ^a	Sulfone ^b
Allyl	920, 992	930, 970	925, 984
Crotyl	962	960	960
α -Methylallyl	915, 985	920, 982	925, 988
Cinnamyl	963	960	960
α -Phenylallyl	920, 985	925, 970	925, 980
α,δ -Dimethylallyl	965	960	960

a - 2,6-Dimethylbenzenesulfinate.

b - 2,6-Dimethylphenyl sulfone.

Bellamy(29) reports the following data for the olefinic infrared absorption in the 900-1000 cm^{-1} region. Trans disubstituted ethylenic double bonds give rise to a strong absorption band in the region 990-965 cm^{-1} . Cis disubstituted ethylenes do not absorb in the region 1000-900 cm^{-1} . Monosubstituted vinyl groups give rise to two strong bands near 990 and 910 cm^{-1} . The band at 910 cm^{-1} is shifted to slightly higher frequencies by polar substituents. For example, the vinyl group of $\text{CH}_2=\text{CHCH}_2\text{OCOR}$ absorbs at 985 and 932 cm^{-1} .

The data presented in Table X are in good agreement with these values. In the case of allyl and α -phenylallyl 2,6-dimethylbenzenesulfonates, the bands at 970 cm^{-1} are actually the result of an overlap between the vinyl absorption and

that characteristic of the sulfinate group, which absorbed in the same region.

The n.m.r. data are presented in Table XI.

In the run using cinnamyl 2,6 -dimethylbenzenesulfinate with 60% ethanol-water as solvent (Table IX), a 75% yield of α -phenylallyl 2,6-dimethylphenyl sulfone was obtained by isolation of the sulfone which crystallized from the solution on cooling. Extraction of the mother liquor after separation of the sulfone by filtration gave another 14% of sulfone, contaminated with only traces of alcohol. The infrared spectrum of this sulfone showed the presence of both allylic isomers, the cinnamyl and α -phenylallyl 2,6-dimethylphenyl sulfones, in roughly equal amounts as indicated by absorption bands at 925, 960 and 980 cm^{-1} , in carbon disulfide solution.

α -Phenylallyl 2,6-dimethylphenyl sulfone was found to undergo considerable solvolysis and rearrangement to the corresponding cinnamyl sulfone, if the reaction solution in which it was formed was heated for more than 10 half-lives. For example, cinnamyl 2,6-dimethylbenzenesulfinate (0.02216 M) in acetic acid with added sodium acetate (0.04828 M), when heated for 150 hours (330 half-lives) at 90.00°, gave approximately 15% of cinnamyl acetate, and a mixture of the two isomeric sulfones, of which 30% was cinnamyl 2,6-dimethylphenyl sulfone. The composition of the sulfone mixture in this case, was determined from its nuclear magnetic resonance spectrum in chloroform solution. In view of these results, a control experiment on the extent of isomerization of α -phenylallyl 2,6-dimethylphenyl sulfone in 60% ethanol-water

TABLE XI

A summary of the n.m.r. spectral data of various allylic alcohols,
2,6-dimethylbenzenesulfonates and 2,6-dimethylphenyl sulfones^a

	N.m.r. absorption, τ units ^b					
	Vinyl CH ₂	CH	-CH ₂ -	Ar-CH ₃	-C ₆ H ₃	-OH
Allyl						
Alcohol	4.6-5.1(m)	3.8-4.4(m)	5.97(s)	-	-	5.42(s)
Ester ^c	4.6-4.9(m)	3.8-4.4(m)	5.52(d)	7.42(s)	2.7-3.2(m)	-
Sulfone ^d	4.7-5.1(m)	4.1-4.5(m)	6.3(d)	7.38(s)	2.7-3.1(m)	-
Crotyl	δ -CH ₃	-CH=CH-	-CH ₂ -	Ar-CH ₃	-C ₆ H ₃	-OH
Alcohol	8.30(d)	4.3-4.5(m)	6.1(s)	-	-	5.7(s)
Ester ^c	8.32(d)	4.3-4.5(m)	5.6(d)	7.43(s)	2.7-3.2(m)	-
Sulfone ^d	8.35(d)	4.5-4.7(m)	6.4(d)	7.38(s)	2.7-3.1(m)	-
α -Methylallyl	Vinyl CH ₂	CH	$>$ CH-	α -CH ₃	Ar-CH ₃	-C ₆ H ₃ -OH
Alcohol	4.7-5.2(m)	3.95-4.4(m)	5.9	8.8(d)	-	5.9
Ester ^c	4.6-5.0(m)	3.95-4.4(m)	5.1-5.5(m)	8.6(d)	7.42(s)	2.7-3.2(m) -
Sulfone ^d	4.8-5.0(m)	4.1-4.5(m)	6.2-6.6(m)	8.55(d)	7.38(s)	2.7-3.0(m) -

Continued next page

TABLE XI - continuation

α, γ -Dimethyl-allyl	α -CH ₃	γ -CH ₃	-CH=CH-	>CH-	Ar-CH ₃	-C ₆ H ₃	-OH
Alcohol	8.86(d)	8.35(d)	4.4-4.6(q)	5.9(t)	-	-	6.15(s)
Ester ^c	8.63(d)	8.30(d)	4.3-4.6(q)	5.1-5.4(t)	7.42(s)	2.9-3.2(m)	-
Sulfone ^d	8.63(d)	8.45(d)	4.6-4.8(q)	6.3-6.7(q)	7.40(s)	2.8-3.0(m)	-
Cinnamyl	γ -C ₆ H ₅	-CH=CH-	-CH ₂ -	Ar-CH ₃	-C ₆ H ₃	-OH	-OH
Alcohol	2.82(s)	3.6-3.8(q)	5.83	-	-	5.8	-
Ester ^c		3.5-3.8(m)	5.4(d)	7.40(s)	2.6-3.2(m)	-	-
Sulfone ^d		3.7-3.9(m)	6.05(d)	7.30(s)	-	-	-
α -Phenylallyl	α -C ₆ H ₅	Vinyl CH ₂ and CH	>CH-	Ar-CH ₃	C ₆ H ₃	-OH	-OH
Alcohol	2.82(s)	4.7-5.2(m)	3.8-4.4(m)	- ^e	-	6.45(s)	-
Ester ^c	2.77(s)	\leftarrow — — — — — \rightarrow	3.8-5.9(m)	7.50(d)	2.8-3.2(m)	-	-
Sulfone ^d		4.4-4.8(m)	3.6-3.8(m)	5.1-5.3(m)	7.42(s)	-	-

a - The solvent for the spectra of cinnamyl and α -phenylallyl 2,6-dimethylphenyl sulfones was chloroform; the solvent for the spectra of all other compounds was carbon tetrachloride.

b - Where s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet.

c - 2,6-Dimethylbenzenesulfinate.

d - 2,6-Dimethylphenyl sulfone.

e - The signal of this proton overlapped with that of the vinyl methylene.

under the conditions employed for rearrangement of cinnamyl 2,6-dimethylbenzenesulfinate was carried out. From a solution of α -phenylallyl 2,6-dimethylphenyl sulfone (0.00804 M) in 60% ethanol-water containing 0.0246 M 2,6-lutidine, which was heated for two hours at 90.00°, 78% of starting material was recovered by filtration after cooling. The infrared spectrum (CS_2) of the residue (12.6%) obtained by extraction of the filtrate, showed the presence of starting material and only traces of the cinnamyl 2,6-dimethylphenyl sulfone.

The reaction of cinnamyl 2,6-dimethylbenzenesulfinate in acetonitrile was also studied. A 98.7% yield of α -phenylallyl 2,6-dimethylphenyl sulfone was obtained from a solution of cinnamyl 2,6-dimethylbenzenesulfinate (0.0175 M) in acetonitrile containing 0.0466 M 2,6-lutidine, which was heated for 45 hours (12 half-lives) at 90.00°. According to the infrared spectrum of the crude product, only traces of the isomeric sulfone might have been present.

The sulfones obtained from the rearrangement of crotyl and cinnamyl 2,6-dimethylbenzenesulfinate in acetic acid, were contaminated with traces of acetate as indicated by a weak infrared band at 1735 cm^{-1} in carbon disulfide. The sulfones formed by the rearrangement of cinnamyl and α -phenylallyl 2,6-dimethylbenzenesulfinate in 60% ethanol-water were contaminated with traces of alcohol as indicated by a very weak infrared absorption at 3600 cm^{-1} (CS_2). In the other runs listed in Table IX, no infrared evidence could be obtained for the formation of solvolysis products. However, it is likely that the allyl,

crotyl and α -methylallyl alcohols, if formed in small quantities, might have been lost during the work up of the reaction mixture. Additional information with regard to the extent solvolysis accompanying the rearrangement of sulfinates to sulfones, is provided by the titrimetric results which are described below.

The results of a number of titrimetric runs, measuring the amount of acid produced during the rearrangement of several allylic 2,6-dimethylbenzenesulfinates in buffered 60% ethanol-water at 90.00°, are reported in Table XII. The acidity change in the case of α -phenylallyl 2,6-dimethylbenzenesulfinate has not been measured.

The acid produced during 10 half-lives, in any of the runs listed in Table XI, sets an upper limit for the amount of solvolysis accompanying rearrangement. The following observations will be of assistance for the assignment of the titrimetric data to sulfur-oxygen or carbon-oxygen bond fission.

In anhydrous ethanol at 90.00°, with added sodium acetate (0.0678 M), allyl 2,6-dimethylbenzenesulfinate (0.03572 M) underwent practically complete sulfur-oxygen bond fission, as evidenced by the formation of ethyl 2,6-dimethylbenzenesulfinate (strong infrared bands at 882, 1015 and 1132 cm^{-1} in CS_2). Only traces of sulfone were formed as indicated by a weak band at 1320 cm^{-1} (CS_2) in the infrared spectrum. No acid was produced in this reaction. The rate constant for the disappearance of allyl 2,6-dimethylbenzenesulfinate (0.0213 M) in anhydrous ethanol with added sodium acetate (0.0456 M) at 90.00°, was equal to $1.79 \pm .06 \times 10^{-5} \text{ sec}^{-1}$ (Run 56). In anhydrous ethanol

TABLE XII

Titrimetric changes accompanying the rearrangement of various

allylic 2,6-dimethylbenzenesulfonates in 60% EtOH-H₂O at 90.00 ± .03°

2,6-Dimethyl- benzenesulfonate	(Ester)M	Added base	(Base), M	t _{1/2} ^a	Time	%Acid formed	%Acid total ^b	Notebook ref.
Allyl	0.0236	NaOAc	0.0473	ca. 42 hrs. ^c	40 hrs.	12	24	179-1
"	0.0231	2,6-Lutidine	0.0507	42 hrs.	101 hrs.	4.5	6	243-1
Crotyl	0.0225	NaOAc	0.0487	70 min.	90 min.	2	3.5	126-1
α-Methylallyl	0.0230	NaOAc	0.0487	ca. 15 min. ^c	30 min.	2	3	177-1
"	0.0292	2,6-Lutidine	0.0509	15 min.	144 min.	1	1	264-1
Cinnamyl	0.0166	NaOAc	0.0368	12 min.	60 min.	6.2	6.4	180-1
"	0.0179	2,6-Lutidine	0.0484	ca. 12 min. ^c	120 min.	5.8	5.8	278-1

a - Obtained from the infrared kinetic data.

b - These values represent the % acid formed after 10 half-lives of reaction. In several cases they were calculated from the values of preceding column.

c - The substitution of sodium acetate for 2,6-lutidine or viceversa is assumed to have no large effect on t_{1/2}.

at 90.00° with 2,6-lutidine present (0.05028 M), allyl 2,6-dimethylbenzenesulfinate (0.02294 M) was found to undergo rearrangement to allyl 2,6-dimethylphenyl sulfone, with no ethyl 2,6-dimethylbenzenesulfinate being discernible by infrared. The rate constant for disappearance of allyl 2,6-dimethylbenzenesulfinate (0.0228 M) in anhydrous ethanol at 90.00°, with added 2,6-lutidine (0.0439 M), was equal to $1.25 \pm .04 \times 10^{-6} \text{ sec}^{-1}$ (Run 55).

The reaction of cinnamyl 2,6-dimethylbenzenesulfinate (0.02514 M) in anhydrous ethanol at 90.00° with added sodium acetate (0.0536 M), afforded a mixture of α -phenylallyl 2,6-dimethylphenyl sulfone and ethyl 2,6-dimethylbenzenesulfinate, the first being the major product. The rate constant for the disappearance of cinnamyl ester (0.0201 M) in anhydrous ethanol at 90.00° with added sodium acetate (0.0458 M) was equal to $1.97 \pm .05 \times 10^{-4} \text{ sec}^{-1}$ (Run 42). There was no infrared evidence for the formation of ethyl 2,6-dimethylbenzenesulfinate from the reaction of cinnamyl 2,6-dimethylbenzenesulfinate (0.01874 M) in anhydrous ethanol at 90.00°, in the presence of 2,6-lutidine (0.0806 M). The rate constant for the disappearance of cinnamyl ester (0.0203 M) in anhydrous ethanol at 90.00° with added 2,6-lutidine (0.0609 M) was equal to $1.73 \pm .03 \times 10^{-4} \text{ sec}^{-1}$ (Run 57). No acid was produced in this run.

B. The relation between the configuration of (+)- α,δ -dimethylallyl 2,6-dimethylbenzenesulfinate and (+)- α,δ -dimethylallyl 2,6-dimethylphenyl sulfone.

In order to establish this relation, optically active 2-pentyl 2,6-dimethylphenyl sulfone was synthesized in a stereo-

specific manner, and its configuration related to that of the corresponding optically active α,δ -dimethylallyl sulfone as described below.

An attempt to resolve 2-pentanol by the method reported by Pickard and Kenyon (37) was unsuccessful due to the failure of 2-pentyl acid phthalate to crystallize. Optically active 2-pentanol was obtained by the hydrolysis of active 2-pentyl acid phthalate, derived from active α,δ -dimethylallyl acid phthalate, previously prepared (Chapter 1).

(+)- α,δ -Dimethylallyl acid phthalate of $[\alpha]_D^{25} +23.34^\circ$ ($\underline{1} = 1$, $\underline{c} = 5$, CHCl_3), was reduced by means of diimide generated from *p*-toluenesulfonylhydrazine(38), to (+)-2-pentyl acid phthalate of $[\alpha]_D^{25} +25.58^\circ$ ($\underline{1} = 1$, $\underline{c} = 5$, CHCl_3). Alkaline hydrolysis of this compound gave (+)-2-pentanol with a specific rotation $[\alpha]_D^{25} +5.42^\circ$ ($\underline{1} = 1$, $\underline{c} = 5$, CHCl_3). As neither the diimide reduction, nor the hydrolysis of the acid phthalate involve the asymmetric centre, the configuration of this alcohol is the same as that of (+)- α,δ -dimethylallyl alcohol.

On treatment of the (+)-2-pentanol thus obtained, with *p*-toluenesulfonyl chloride in pyridine at -5° , (+)-2-pentyl *p*-toluenesulfonate was obtained, $[\alpha]_D^{25} +4.38^\circ$ ($\underline{1} = 1$, $\underline{c} = 5$, CHCl_3). This compound was allowed to react with an ethanolic solution of sodium 2,6-dimethylthiophenoxide, and afforded (+)-2-pentyl 2,6-dimethylphenyl sulfide, $[\alpha]_D^{25} +1.25^\circ$ ($\underline{1} = 1$, $\underline{c} = 19.15$, CHCl_3). On oxidation of this active sulfide with hydrogen peroxide in acetic acid, (+)-2-pentyl 2,6-dimethylphenyl sulfone was obtained, $[\alpha]_D^{25} +22.0^\circ$ ($\underline{1} = 1$, $\underline{c} = 2.5$, CHCl_3).

Of the last three reactions there is only one involving the asymmetric carbon, the displacement of the *p*-toluenesulfonate group by 2,6-dimethylthiophenoxide ion. This reaction should proceed with inversion of configuration(39). The configuration of the (+)-2-pentyl 2,6-dimethylphenyl sulfone should therefore be inverted with respect to that of (+)-2-pentanol as well as to that of (+)- α,γ -dimethylallyl alcohol, since the configurations of the last two compounds are the same.

(+)- α,γ -Dimethylallyl 2,6-dimethylphenyl sulfone, $[\alpha]_D^{25} +7.02^\circ$ ($\underline{1} = 1$, $\underline{c} = 4.9$, CHCl_3), obtained from the rearrangement of (+)- α,γ -dimethylallyl 2,6-dimethylbenzenesulfinate(Chapter 1), was reduced with diimide generated from *p*-toluenesulfonylhydrazine to (+)-2-pentyl 2,6-dimethylphenyl sulfone, $[\alpha]_D^{25} +22.6^\circ$ ($\underline{1} = 1$, $\underline{c} = 2.1$, CHCl_3). Repetition of the reduction gave (+)-2-pentyl 2,6-dimethylphenyl sulfone $[\alpha]_D^{25} +20.2^\circ$ ($\underline{1} = 1$, $\underline{c} = 2.1$, CHCl_3 .)

As the diimide reduction does not affect the asymmetric carbon, this result indicates that (+)- α,γ -dimethylallyl 2,6-dimethylphenyl sulfone has the same configuration as that of (+)-2-pentyl 2,6-dimethylphenyl sulfone. Since the configuration of (+)-2-pentyl 2,6-dimethylphenyl sulfone is inverted with respect to that of (+)- α,γ -dimethylallyl alcohol, it follows that the configuration of (+)- α,γ -dimethylallyl 2,6-dimethylphenyl sulfone must also be inverted with respect to that of (+)- α,γ -dimethylallyl alcohol.

Finally, the conversion of (+)- α,γ -dimethylallyl alcohol to (+)- α,γ -dimethylallyl 2,6-dimethylbenzenesulfinate proceeds with retention of configuration, and therefore the rearrangement of this sulfinate ester to the (+)- α,γ -dimethylallyl

2,6-dimethylphenyl sulfone takes place with inversion of configuration.

C. A kinetic study of the rearrangement of various allylic 2,6-dimethylbenzenesulfinates.

All the kinetic data to be mentioned in this section have been obtained spectrophotometrically by following the rate of disappearance of a characteristic sulfinates absorption band in the infrared. Control runs on the extraction procedure and the adherence of the ester bands to the Lambert-Beer law were carried out according to the method described in Chapter 1. The results of these control runs for allyl, crotyl, α -methylallyl, cinnamyl and α -phenylallyl, appearing in Figs. 4-6, show good linearity.

The kinetic data for the rearrangement of allyl, crotyl, α -methylallyl, cinnamyl and α -phenylallyl 2,6-dimethylbenzenesulfinates in two or more solvents are listed in Table XIII. Sample rate runs for each ester with corresponding plots of $\log A_{\text{obs.}}$ versus time, to illustrate the method of calculation of the data in Table XIII, are illustrated in Tables XIV - XVIII and Figs. 7-11.

α -Methylallyl and α -phenylallyl 2,6-dimethylbenzenesulfinates contained an asymmetric carbon atom and as a result of this, the initial esters consisted of a mixture of two racemic diastereomers. As in the case of α,γ -dimethylallyl 2,6-dimethylbenzenesulfinate, plots of $\log A_{\text{obs.}}$ versus time for these two esters (Figs. 9 and 11, respectively) yield curves from which the rates of both slow and fast diastereomer can be calculated in the same manner as employed for the α,γ -dimethylallyl 2,6-dimethylbenzenesulfinate. This is shown in Tables XVI and XVIII for

Relative concentration

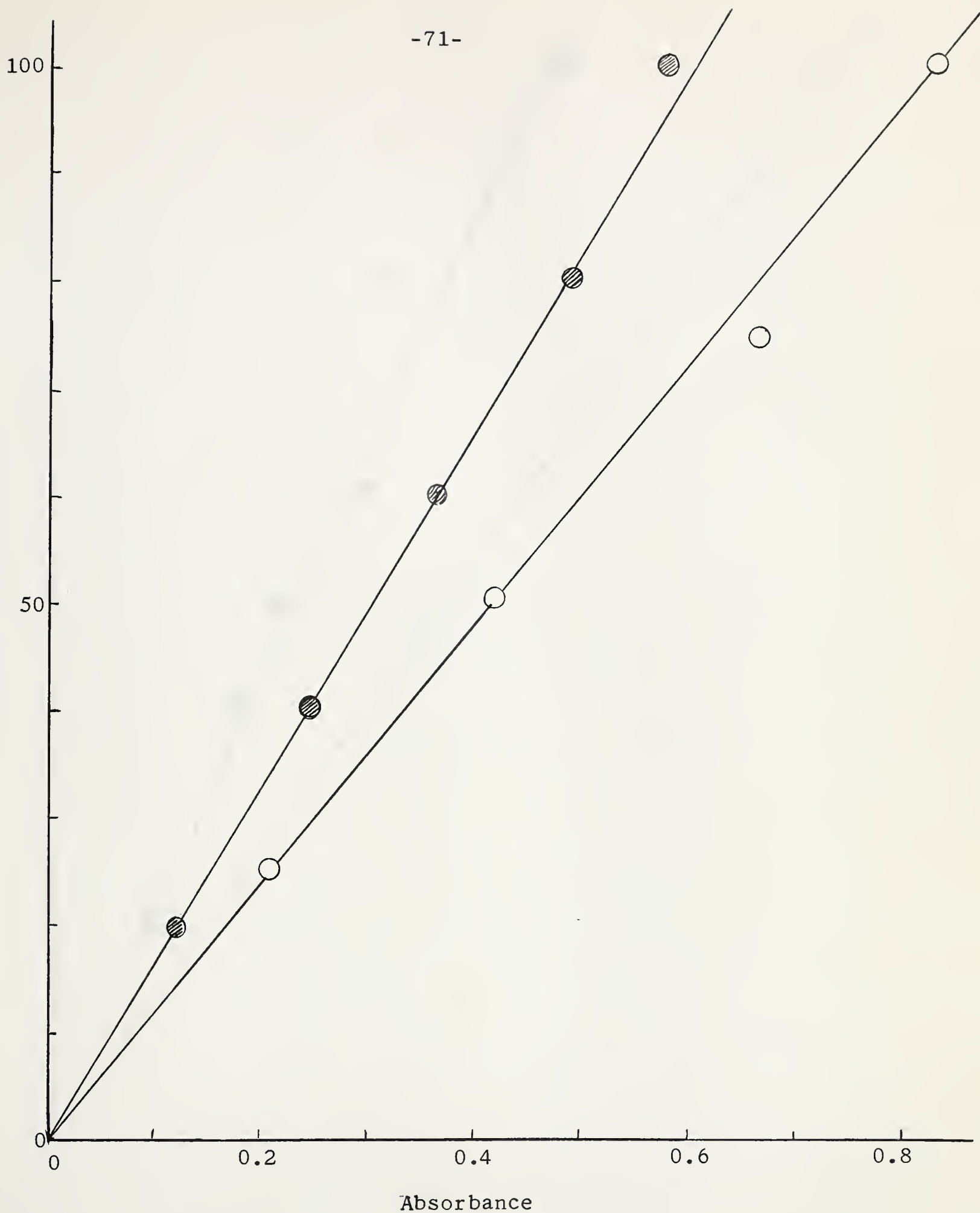


Fig. 4 - Lambert-Beer law and extraction procedure control for allyl and crotyl 2,6-dimethylbenzenesulfonates (○ - allyl, 100 \equiv 0.0229 M; \otimes - crotyl, 100 \equiv 0.02126 M).

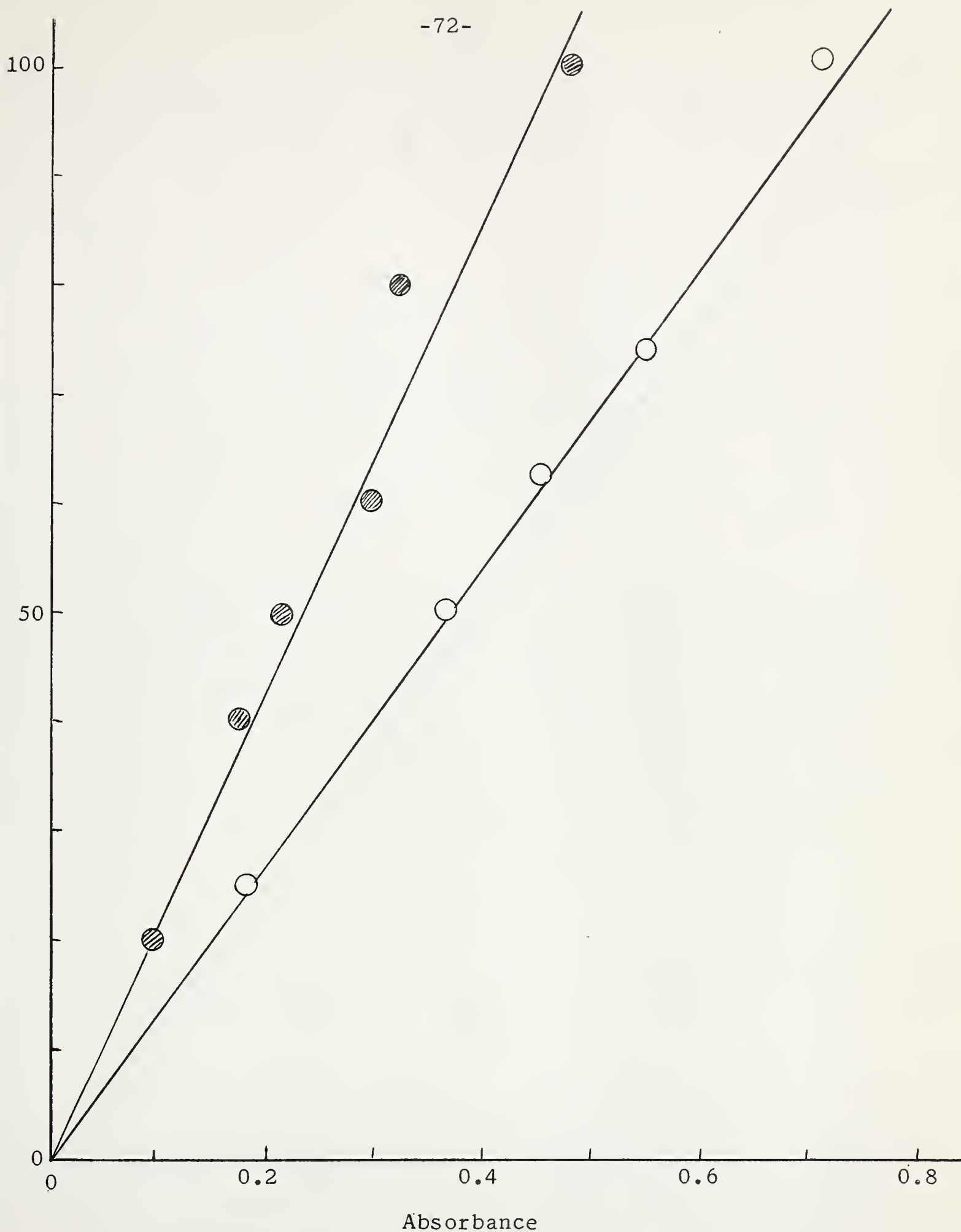


Fig. 5 - Lambert-Beer law and extraction procedure control for α -methylallyl and α -phenylallyl 2,6-dimethylbenzenesulfonates (\bigcirc - α -methylallyl, 100 \equiv 0.0255 M; $\textcircled{/}$ - α -phenylallyl, 100 \equiv 0.0206 M).

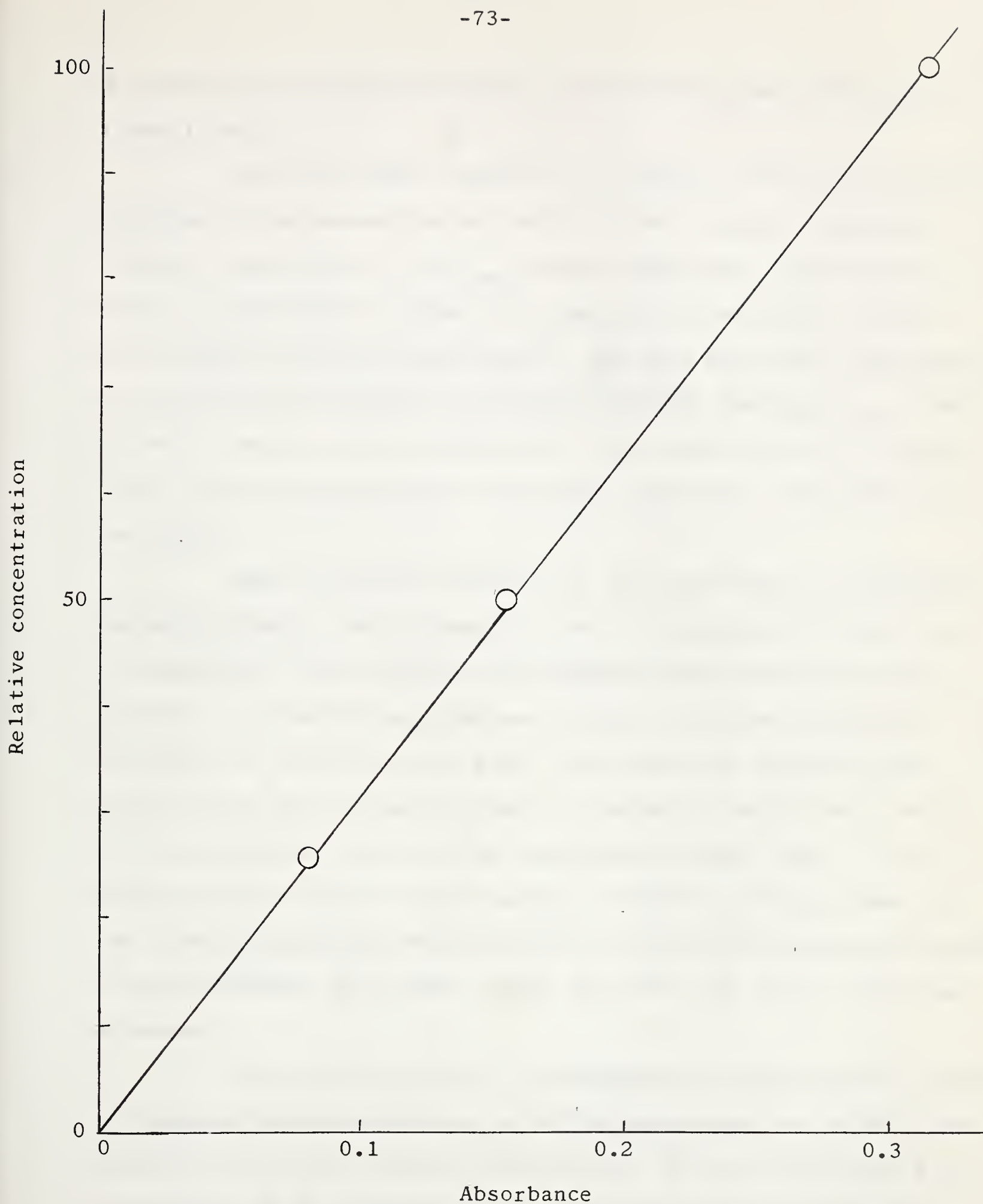


Fig. 6 - Lambert-Beer law and extraction procedure control for cinnamyl 2,6-dimethylbenzenesulfinate ($100 \equiv 0.02014 \text{ M}$).

α -methylallyl and α -phenylallyl 2,6-dimethylbenzenesulfonates, respectively.

With the other esters, i.e., allyl, crotyl, and cinnamyl 2,6-dimethylbenzenesulfonates, which do not contain asymmetric centers, the plots of $\log A_{\text{obs.}}$ versus time show good linearity. This is illustrated in Figs. 7, 8 and 10 for the allyl, crotyl and cinnamyl esters, respectively. The data were then substituted in the first-order kinetic expression $k = 2.303/t \log(A_0/A)_{\text{obs.}}$, where A_0 and A are the absorbances at zero time and at time t , respectively, for the calculation of the rate constants (Tables XIV, XV, and XVII).

Due to the fast reaction of α -phenylallyl 2,6-dimethylbenzenesulfonate, the accuracy of the rate constants for the rearrangement of this compound is somewhat lower than the average accuracy. In Run 23 using α -methylallyl 2,6-dimethylbenzenesulfonate in solvent acetic acid, there were not enough points taken in the early stage of reaction and as a result the rate of fast diastereomer could not be determined in this case. It was found that the rate of rearrangement of the fast diastereomer of the α -methylallyl and α -phenylallyl 2,6-dimethylbenzenesulfonates is approximately four times faster than the rate of the slow diastereomer.

The relative rates of rearrangement of the various allylic 2,6-dimethylbenzenesulfonates in 60% ethanol-water at 90.00°, are shown in the second column of Table XIX. The rate constants for reaction of α, δ -dimethylallyl and α -phenylallyl 2,6-dimethylbenzenesulfonates were not measured at 90.00°. The rate constant for the former compound was obtained by extrapolation of data at lower temperatures (25.00° and 70.00°). The rate constant

TABLE XIII

Rate constants for the rearrangement of various allylic 2,6-dimethylbenzenesulfonates
to allylic 2,6-dimethylphenyl sulfones

Run #	2,6-Dimethyl- benzenesulfonate	Solvent	Temp., °C.	(Ester), M	(Base), M	k x 10 ⁴ , sec ⁻¹ ^a	Notebook ref.
29	Allyl	AcOH	90	0.0260	0.0516 ^b	0.0635+ .003	130-1
21	"	60% EtOH-H ₂ O	90	0.0218	0.0514 ^b	0.0457+ .002	101-1
22	Crotyl	AcOH	90	0.0222	0.0500 ^b	0.937+ .042	111-1
24	"	60%EtOH-H ₂ O	90	0.0225	0.0487 ^c	1.66+ 0.07	122-1
23	α-Methylallyl	AcOH	90	0.0222	0.0501 ^b	3.94+ 0.13	113-1
25	"	60%EtOH-H ₂ O	90	0.0227	0.0497 ^b	6.45+ .15 (23.5+ .7)	117-1
41	Cinnamyl	AcOH	90	0.0213	0.0540 ^c	4.24+ 0.19	164-1
40	"	60%EtOH-H ₂ O	90	0.0215	0.0500	10.1+ .6	162-1
26	α-Phenylallyl	AcOH	22	0.0243	0.0489 ^b	1.88+ .07 (10.6+ .6)	120-1
27	"	60%EtOH-H ₂ O	25	0.0243	0.0487 ^c	3.26 (12.0)	127-1
32	"	Acetonitrile	70	0.0214	0.0574 ^b	11.1 (46.5)	145-1
33	"	Cyclohexane	70	0.0199	0.0563 ^b	0.737+ .001 (1.74+ 0.22)	146-1

a - The values appearing in brackets are the rate constant for the fast reacting diastereomer.

b - 2,6-Lutidine.

c - Sodium acetate.

TABLE XIV

Calculations for the determination of the rate constant
for the rearrangement of allyl 2,6-dimethylbenzene-
sulfinate in 60% EtOH-H₂O at 90.00 ± 0.03°

Run #21. (Ester) = 0.0218 M; (2,6-Lutidine) = 0.0514 M.

Time, hr.	$\text{Log} \frac{I_0}{I} = A_{\text{obs.}}$	$\text{Log} A_{\text{obs.}}$	$\text{Log}(A_0/A)_{\text{obs.}}$	$k \times 10^6,$ sec^{-1}
0	0.7705	1.8868	-	-
17	0.5911	1.7717	0.1151	4.29
41	0.3963	1.5980	0.2888	4.49
64	0.2457	1.3904	0.4964	4.95
89	0.1719	1.2353	0.6515	4.69
114	0.1253	1.0979	0.7889	4.43

Average value of $k = 4.57 \pm 0.20 \times 10^{-6} \text{ sec}^{-1}$

TABLE XV

Calculations for the determination of the rate constant
for the rearrangement of crotyl 2,6-dimethylbenzene-
sulfinate in 60% EtOH-H₂O at 90.00 \pm 0.03°

Run #24. (Ester) = 0.0225 M; (NaOAc) = 0.0487 M.

Time, min.	$\text{Log} \frac{I_0}{I} = A_{\text{obs.}}$	$\text{Log} A_{\text{obs.}}$	$\text{Log}(A_0/A)_{\text{obs.}}$	$k \times 10^4,$ sec^{-1}
0	0.4485	$\bar{1}.6518$	-	-
13	0.4121	$\bar{1}.6150$	0.0368	1.09
30	0.3283	$\bar{1}.5163$	0.1355	1.73
63	0.2425	$\bar{1}.3847$	0.2671	1.63
90	0.1766	$\bar{1}.2470$	0.4048	1.73
140	0.1218	$\bar{1}.0856$	0.5662	1.55

Average value of $k = 1.66 \pm 0.07 \times 10^{-4} \text{ sec}^{-1}$

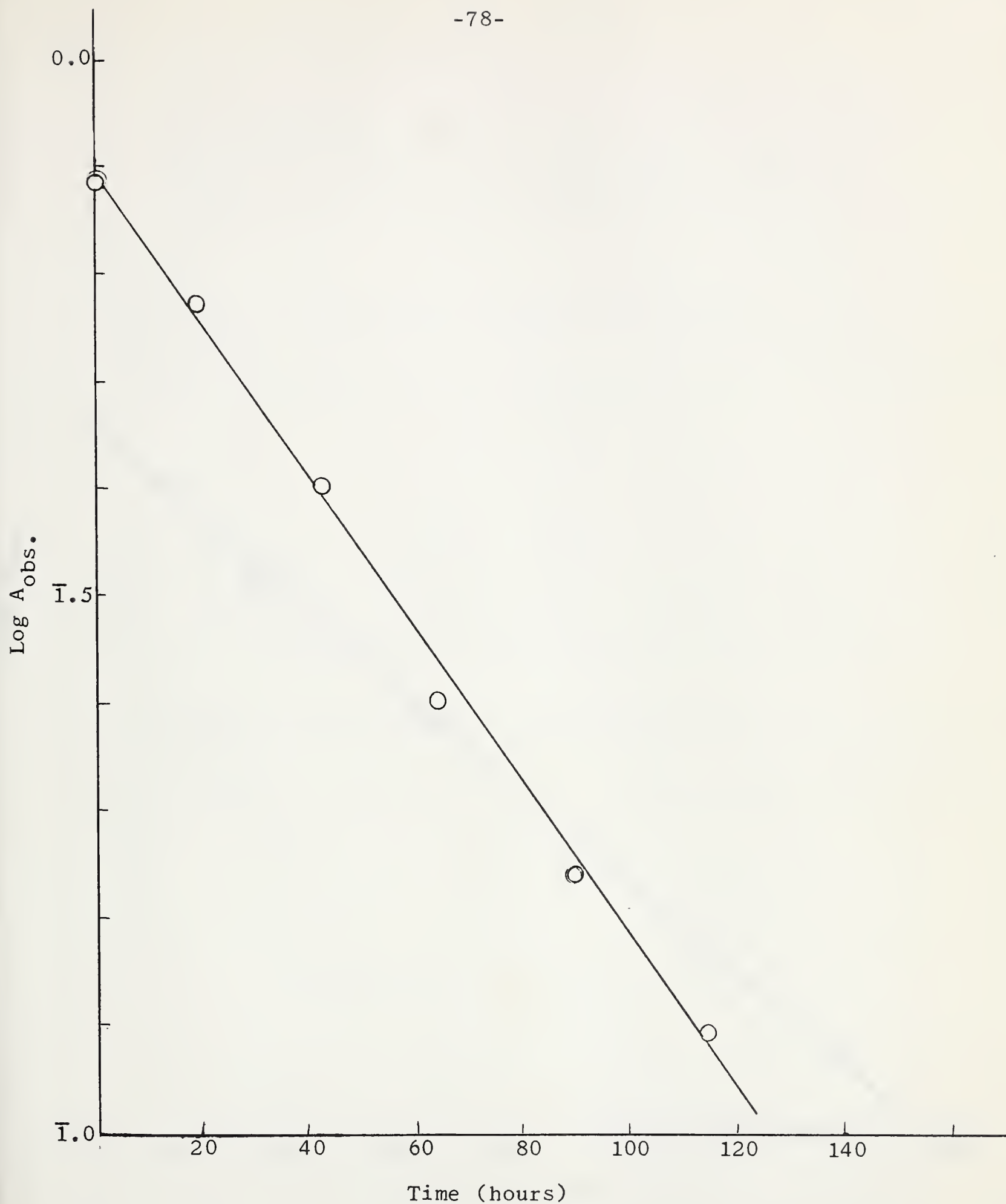


Fig. 7 - Plot of logarithm of absorbance of ester vs. time for the rearrangement of allyl 2,6-dimethylbenzenesulfinate to sulfone in 60% EtOH-H₂O at 90.00° (Table XIV).

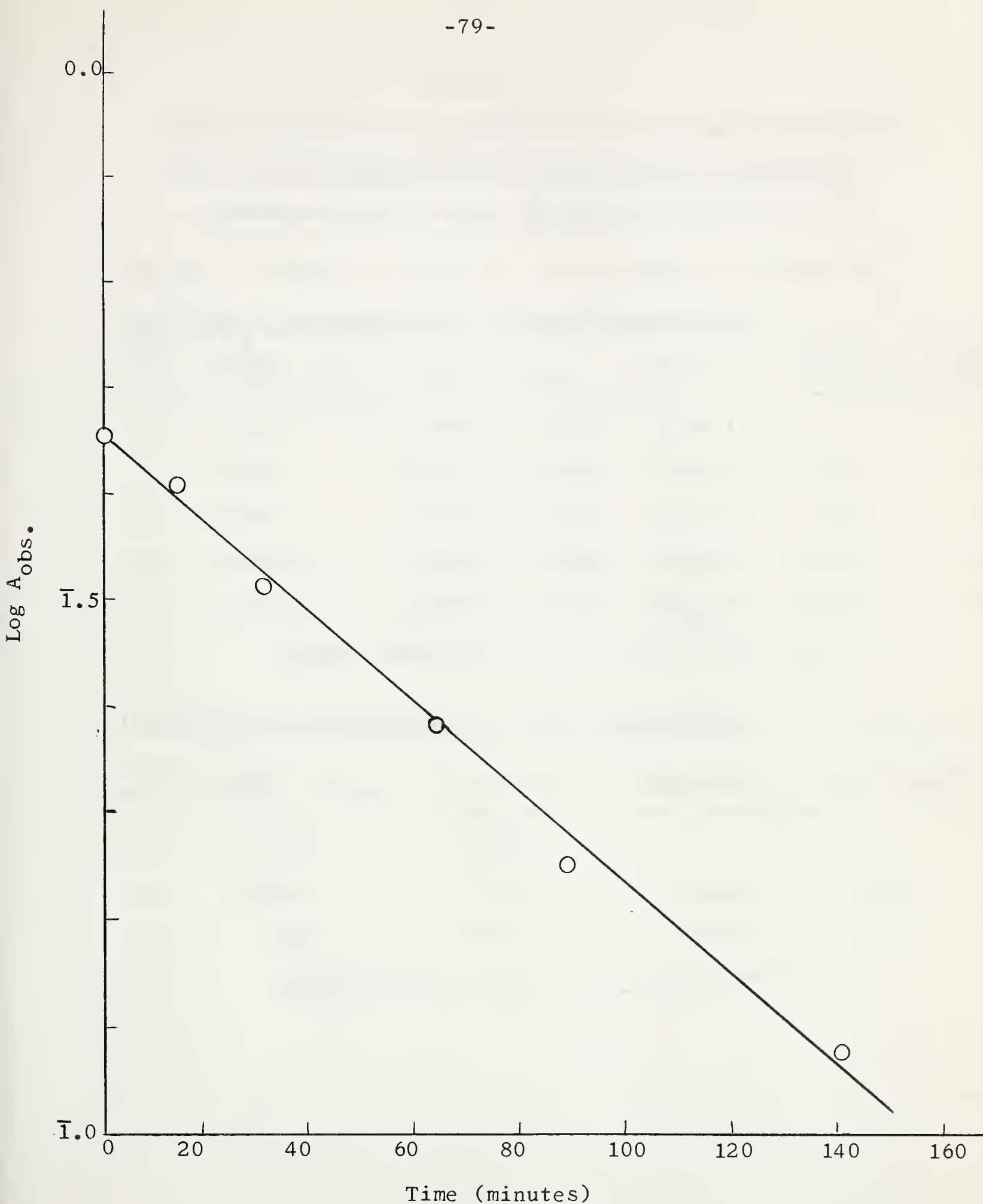


Fig. 8 - Plot of logarithm of absorbance of ester vs. time for the rearrangement of crotyl 2,6-dimethylbenzenesulfinate to sulfone in 60% EtOH-H₂O at 90.00° (Table XV).

TABLE XVI

Calculations for the determination of the rate constant
for the rearrangement of α -methylallyl 2,6-dimethyl-
benzenesulfinate in 60% EtOH-H₂O at 90.00 \pm 0.03°

Run #25. (Ester) = 0.0227 M; (2,6-Lutidine) = 0.0497 M.

(a) Rate of disappearance of fast diastereomer

Time, min.	$\text{Log} \frac{I_0}{I} = A_{\text{obs.}}$	$A_{\text{ext.}}$	$A_{\text{calc.}}$	$\text{Log} A_{\text{calc.}}$	$\text{Log} \left(\frac{A_0}{A} \right)_{\text{calc.}}$	$k \times 10^4$ sec^{-1}
0	0.5103	0.3864	0.1239	$\bar{1}.0931$	-	-
4	0.4034	0.3312	0.0722	$\bar{2}.8585$	0.2346	22.5
7	0.3480	0.2952	0.0528	$\bar{2}.7226$	0.3705	20.2
10	0.2933	0.2643	0.0290	$\bar{2}.4624$	0.6307	24.2
15	0.2332	0.2187	0.0145	$\bar{2}.1614$	0.9317	23.8

Average value of $k = 23.5 \pm 0.7 \times 10^{-4} \text{ sec}^{-1}$

(b) Rate of disappearance of slow diastereomer

Time, min.	$\text{Log} \frac{I_0}{I} = A_{\text{obs.}}$	$\text{Log} A_{\text{obs.}}$	$\text{Log} (A_0/A)_{\text{obs.}}$	$k \times 10^4, \text{sec}^{-1}$
20	0.1816	$\bar{1}.2591$	-	-
30	0.1222	$\bar{1}.0871$	0.1720	6.60
50	0.0585	$\bar{2}.7672$	0.4919	6.29

Average value of $k = 6.45 \pm 0.15 \times 10^{-4} \text{ sec}^{-1}$

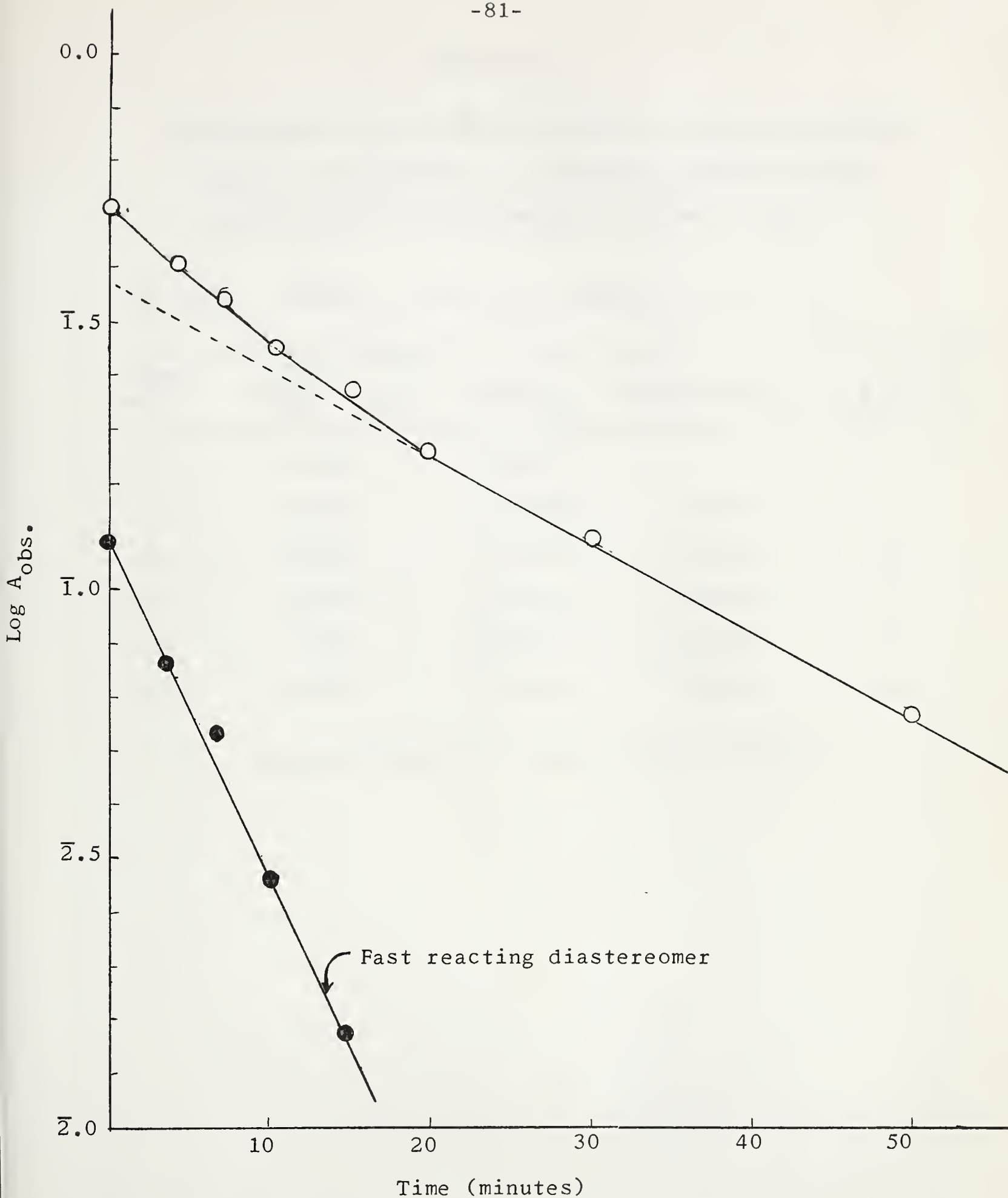


Fig. 9 - Plot of logarithm of absorbance of ester vs. time for the rearrangement of α -methylallyl 2,6-dimethylbenzenesulfinate to sulfone in 60% EtOH-H₂O at 90.00° (Table XVI).

TABLE XVII

Calculations for the determination of the rate constant
for the rearrangement of cinnamyl 2,6-dimethylben-
zenesulfinate in 60% EtOH-H₂O at 90.00 \pm 0.03°

Run #40. (Ester) = 0.0215 M; (NaOAc) = 0.0500 M.

Time, min.	$\text{Log} \frac{I_0}{I} = A_{\text{obs.}}$	$\text{Log } A_{\text{obs.}}$	$\text{Log}(A_0/A)_{\text{obs.}}$	$k \times 10^3,$ sec^{-1}
0	0.3076	$\bar{1}.4880$	-	-
5	0.2207	$\bar{1}.3438$	0.1442	1.11
10	0.1690	$\bar{1}.2279$	0.2601	1.00
15	0.1176	$\bar{1}.0704$	0.4176	1.07
25	0.0714	$\bar{2}.8537$	0.6341	0.97
30	0.0472	$\bar{2}.6739$	0.8141	0.89

Average value of $k = 1.01 \pm 0.06 \times 10^{-3} \text{ sec}^{-1}$

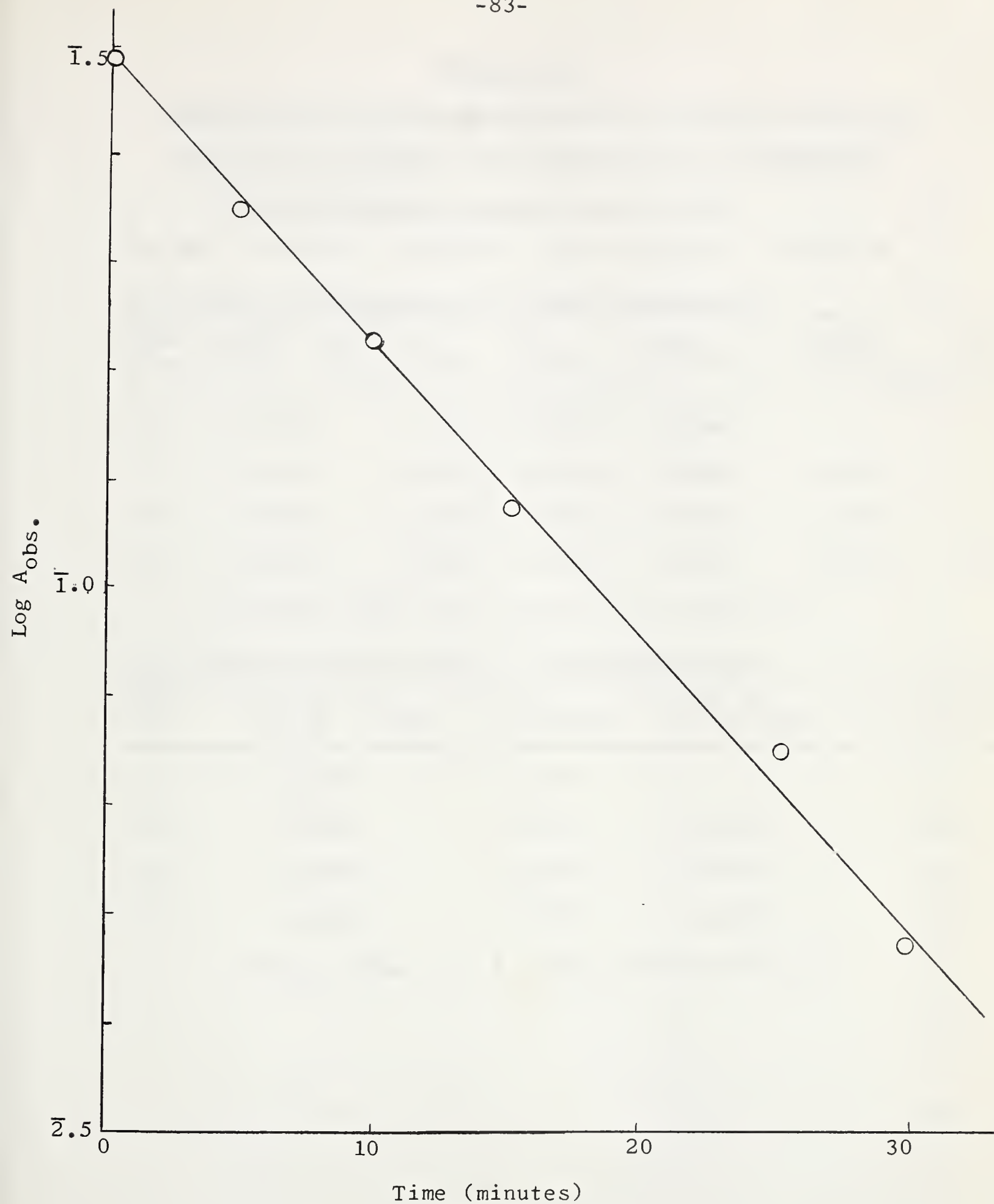


Fig. 10 - Plot of logarithm of absorbance of ester vs. time for the rearrangement of cinnamyl 2,6-dimethylbenzenesulfinate to sulfone in 60% EtOH-H₂O at 90.00° (Table XVII).

TABLE XVIII

Calculations for the determination of the rate constant
for the rearrangement of α -phenylallyl 2,6-dimethyl-
benzenesulfinate in acetic acid at 22°

Run #26. (Ester) = 0.0243 M; (2,6-Lutidine) = 0.0489 M.

(a) Rate of disappearance of fast diastereomer

Time, min.	$\text{Log} \frac{I_0}{I} = A_{\text{obs.}}$	$A_{\text{ext.}}$	$A_{\text{calc.}}$	$\text{Log} A_{\text{calc.}}$	$\text{Log} \left(\frac{A_0}{A} \right)_{\text{calc.}}$	$k \times 10^4$ sec^{-1}
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0	0.4720	0.3177	0.1543	$\bar{1}.1884$	-	-
5	0.4140	0.2985	0.1155	$\bar{1}.0625$	0.1259	9.7
10	0.3614	0.2819	0.0795	$\bar{2}.9004$	0.2880	11.1
21	0.2847	0.2471	0.0376	$\bar{2}.5752$	0.6132	11.2

Average value of $k = 10.6 \pm .7 \times 10^{-4} \text{ sec}^{-1}$

(b) Rate of disappearance of slow diastereomer

Time, min.	$\text{Log} \frac{I_0}{I} = A_{\text{obs.}}$	$\text{Log} A_{\text{obs.}}$	$\text{Log} (A_0/A)_{\text{obs.}}$	$k \times 10^4, \text{sec}^{-1}$
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30	0.2178	$\bar{1}.3381$	-	-
40	0.2058	$\bar{1}.3135$	0.0246	0.92
50	0.1752	$\bar{1}.2435$	0.0946	1.82
120	0.0760	$\bar{2}.8808$	0.4573	1.95

Average value of $k = 1.88 \pm 0.07 \times 10^{-5} \text{ sec}^{-1}$

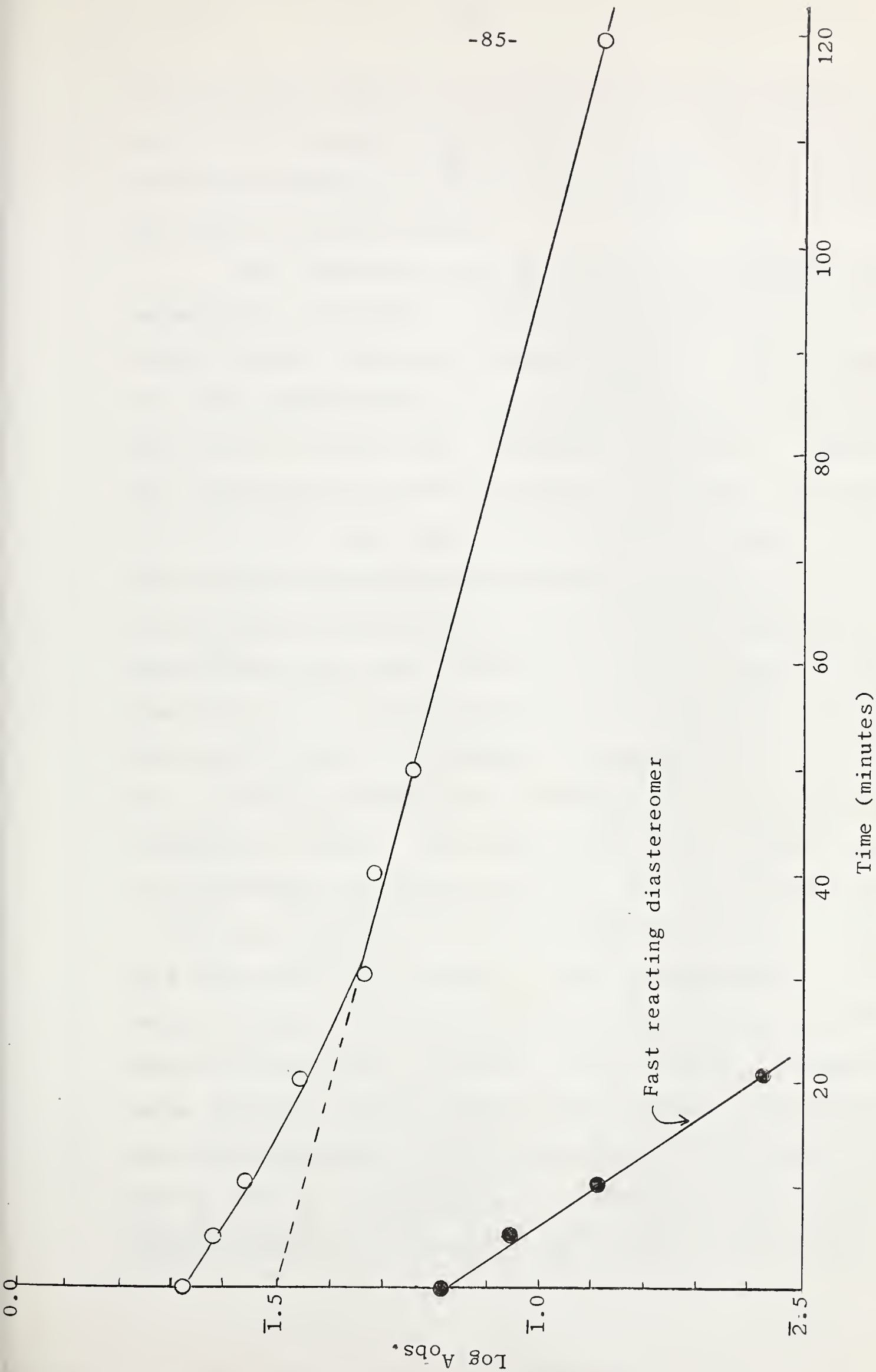


Fig. 11 - Plot of logarithm of absorbance of ester vs. time for the rearrangement of α -phenylallyl 2,6-dimethylbenzenesulfonate in acetic acid at 22°C (Table XVIII).

for the latter compound was assumed to be eight times as large as that for the α,δ -dimethylallyl ester. This factor was found at 25° and would be strictly correct only if both reactions have the same activation energy.

For comparison (see Discussion), the relative rates of unimolecular solvolysis of allylic chlorides at 44.6° in 99.5% formic acid(8), and those of rearrangement of allylic thiocyanates (4b) and thionbenzoates(5) in acetonitrile at 60° and 100°, respectively, have also been included in Table XIX. Except for α,δ -dimethylallyl and α -phenylallyl chlorides, the values listed for the other chlorides have been reported by Vernon(8). Not all the values given by Vernon were actually found in 99.5% formic acid, but only those of the first three compounds. The other three values were derived from data obtained in 50% aqueous ethanol at 0°, as the reaction of these compounds in 99.5% formic acid was too fast to be measured conveniently(8). The relative rates of α,δ -dimethylallyl and α -phenylallyl chlorides were obtained as follows. The rate of solvolysis of α,δ -dimethylallyl chloride in ethanol at 25° ($k = 6.6 \times 10^{-5} \text{ sec}^{-1}$; Ref. 1, p. 786) was compared with that of α,α -dimethylallyl chloride ($k = 1.8 \times 10^{-5} \text{ sec}^{-1}$) under the same conditions (40). The factor between the two was multiplied with the rate of α,α -dimethylallyl chloride relative to allyl chloride, yielding the value listed for α,δ -dimethylallyl chloride. The relative rate of α -phenylallyl chloride was similarly derived by comparing the rate of racemization of (+)- α -phenylallyl chloride in ethanol at 30° ($k = 1.1 \times 10^{-3} \text{ sec}^{-1}$, Ref. 41) with that of

TABLE XIX

Relative rates of reaction of allylic 2,6-dimethylbenzenesulfonates, chlorides, thiocyanates and thionbenzoates

	2,6-Dimethyl- benzenesulfinate ^a	Chloride ^b	Thiocyanate ^c	Thionbenzoate ^d
Allyl	1	1	1	1
Crotyl	36	3.5×10^3	15	6
α -Methylallyl	141	5.67×10^3	-	52
Cinnamyl	221	$\text{ca. } 5 \times 10^5$	-	-
γ, δ -Dimethylallyl	-	$\text{ca. } 1.5 \times 10^7$	150	-
α, α -Dimethylallyl	-	$\text{ca. } 8 \times 10^7$	-	-
α, δ -Dimethylallyl	2.6×10^3	$\text{ca. } 3 \times 10^8$ ^e	-	-
α -Phenylallyl	$\text{ca. } 2.1 \times 10^4$	$\text{ca. } 2 \times 10^9$ ^e	-	-

a - The relative rates are based on the rate of rearrangement of allyl 2,6-dimethylbenzenesulfinate in 60% ethanol-water at 90.00°, $k = 4.57 \times 10^{-6} \text{ sec}^{-1}$ (see text).

b - Data taken from Ref. 8.

c - These values are based on the rate of allyl thiocyanate in acetonitrile at 60°, $k = 1.8 \times 10^{-5} \text{ sec}^{-1}$. Data of Ref. 4b.

d - Allyl thionbenzoate in acetonitrile at 100° has $k = 5.67 \times 10^{-5} \text{ sec}^{-1}$. Data of Ref. 5.

e - These values were derived from data obtained in ethanol solvent (see text).

solvolysis of α,α -dimethylallyl chloride in ethanol at 25° ($k = 1.8 \times 10^{-5} \text{ sec}^{-1}$, Ref. 40) and also making a temperature correction by a factor of 2.5 for the difference in temperature between 30° and 25°.

From the kinetic data for the rearrangement of allylic sulfates at two different temperatures, the activation energies and activation entropies could be calculated. The results are shown in Table XX. With the exception of α -phenylallyl sulfate, the solvent employed for all esters was 60% ethanol-water. Because of the high reactivity of α -phenylallyl sulfate in this solvent, it was substituted by cyclohexane. The enthalpies of activation were calculated from $\Delta H^\ddagger = E_a - RT$, and in turn E_a values were calculated by the Arrhenius equation, $E_a = (2.303 RT_1 T_2 / T_2 - T_1) \log k_2 / k_1$. The entropies of activation were calculated by the Eyring equation, $k = (k' T / h) e^{\Delta S^\ddagger / R} \cdot e^{-\Delta H^\ddagger / RT}$,

TABLE XX

Enthalpies and entropies of activation for the rearrangement
of various allylic 2,6-dimethylbenzenesulfonates^a

Run #	2,6-Dimethyl- benzenesulfonate	Temp., °C.	(Ester), M	(Base), M	k x 10 ⁵ sec ⁻¹	ΔH^\ddagger kcal/mole	ΔS^\ddagger e.u.	Notebook ref.
21	Allyl	90	0.0218	0.0514 ^b	0.457 \pm .02			
37	"	138	0.0226	0.0493 ^b	19.0 \pm 1.1	22.3	-21.9	155-1
36	Crotyl	70	0.0232	0.0484 ^c	2.66 \pm .07			
24	"	90	0.0225	0.0487 ^c	16.6 \pm .7	21.9	-15.9	154-1
35	α -Methylallyl	70	0.0234	0.0486 ^b	8.89 \pm .31			
25	"	90	0.0227	0.0497 ^b	64.5 \pm 1.5	23.8	-8.1	153-1
43	Cinnamyl	70	0.0190	0.0441 ^c	21.5 \pm 1.2			
40	"	90	0.0215	0.0500 ^c	101.0 \pm 6.0	18.4	-21.9	176-1
45	α,γ -Dimethylallyl	25	0.0244	0.0496 ^c	4.09			
18	"	70	0.0206	0.0495 ^b	265 \pm 16	18.1	-17.7	184-1
33	α -Phenylallyl	70	0.0199	0.0563 ^b	7.37 \pm 0.01			
34	"	90	0.0218	0.0510 ^b	43.5 \pm 2.2	21.3	-15.9	148-1

a - The solvent for all esters except α -phenylallyl sulfonate was 60% ethanol-water. The solvent for α -phenylallyl ester was cyclohexane. In the case of α -methylallyl, α,γ -dimethylallyl and α -phenylallyl esters the rate of slow reacting diastereomer is recorded.

b - 2,6-Lutidine.

c - Sodium acetate.

DISCUSSION

A. Rearrangement and solvolysis products.

Reference to the data in Table IX shows that the rearrangement of allyl, crotyl, α -methylallyl, cinnamyl and α -phenylallyl 2,6-dimethylbenzenesulfonates to sulfones occurs readily under solvolytic conditions. The sulfones were isolated in each case in greater than 72% yield. No solvolysis products were isolated in the runs of allyl, crotyl and α -methylallyl esters using 60% ethanol-water as solvent. However, it is likely that the parent alcohols or their ethyl ethers, if formed, might have been lost during the process of product isolation. In the runs of crotyl and cinnamyl esters using acetic acid as solvent, and in the runs of cinnamyl and α -phenylallyl esters using 60% ethanol-water as solvent, traces of acetate and alcohols were detected by infrared spectroscopy. Additional information with regard to the extent solvolysis taking place during the rearrangement of the various sulfonate esters in 60% ethanol-water can be obtained from the titrimetric results in this solvent (Table XII). The acid produced in 10 half-lives may be considered as an upper limit to the amount of solvolysis in any run. Examination of the data of Table XII indicates that allyl 2,6-dimethylbenzenesulfonate in 60% ethanol-water with added sodium acetate, may undergo as much as 24% solvolysis, while the extent of solvolysis in the other runs cannot exceed 6.4%.

In aqueous hydroxylic solvents, both carbon-oxygen and sulfur-oxygen bond fission will produce acid. The decision with regard to which of the two processes is responsible for the

observed titrimetric results in the present case, is based on the following considerations. The formation of ethyl 2,6-dimethylbenzenesulfinate from the reaction of allyl 2,6-dimethylbenzenesulfinate in anhydrous ethanol with added sodium acetate at 90.00°, is unequivocal evidence for sulfur-oxygen bond fission ($k = 1.79 \pm .06 \times 10^{-5} \text{ sec}^{-1}$). However, in the presence of 2,6-lutidine instead of sodium acetate, allyl 2,6-dimethylbenzenesulfinate in anhydrous ethanol at 90.00°, underwent rearrangement to the corresponding sulfone with no ethyl 2,6-dimethylbenzenesulfinate being discernible in the infrared spectrum ($k = 1.25 \pm .04 \times 10^{-6} \text{ sec}^{-1}$).

Noreyko(24) has studied the relative rates of sulfur-oxygen bond fission in a number of solvents with various added bases. He found that in anhydrous ethanol using *p*-methoxyneophyl 2,6-dimethylbenzenesulfinate as substrate, sulfur-oxygen bond fission was 10^3 times faster in the presence of potassium acetate than in the presence of 2,6-lutidine. If this same factor is applied to the relative rates of sulfur-oxygen bond fission using allyl 2,6-dimethylbenzenesulfinate as substrate, it can be estimated that the rate of ester disappearance would be ca. $1.8 \times 10^{-8} \text{ sec}^{-1}$, with 2,6-lutidine as added base. Thus, only ca. 1.5% of sulfur-oxygen bond fission would have occurred under these conditions.

By considering the effect of solvent ionizing power on the rate of bimolecular nucleophilic substitution reactions(42), it may be anticipated that a change of solvent from ethanol to 60% ethanol-water will decrease the rate of sulfur-oxygen bond fission by acetate ion, and increase that by 2,6-lutidine. This

prediction is confirmed by the data of Noreyko(24) who has found that the acetate catalyzed sulfur-oxygen bond fission of *p*-methoxyneophyl 2,6-dimethylbenzenesulfinate at 90° is 15 times faster in anhydrous ethanol than in 60% ethanol-water, while that catalyzed by 2,6-lutidine is 12 times faster in 60% ethanol-water than in anhydrous ethanol. As a result, in 60% ethanol-water acetate anion was only 6.5 times more efficient than 2,6-lutidine at producing sulfur-oxygen bond fission.

With allyl 2,6-dimethylbenzenesulfinate, in passing to 60% ethanol-water in the presence of acetate ion, it may be expected that the rate of sulfur-oxygen bond cleavage will be depressed while the rate of sulfone formation enhanced, and as a result a mixture of sulfone and solvolysis products will be formed. This was actually observed. Only 24% of the theoretical amount of acid was produced, the remainder of the reaction produced sulfone. When 2,6-lutidine was used as base, 6% of the theoretical amount of acid was produced (Table XII). The factor of 4 between the two titers is comparable to the factor of 6.5 obtained by Noreyko (24). This evidence tends to suggest that the acid produced during the rearrangement of the allyl ester is due to sulfur-oxygen bond fission rather than to carbon-oxygen bond fission.

Similarly, in the case of α -methylallyl 2,6-dimethylbenzenesulfinate using 60% ethanol-water as solvent, the acid produced changes from 3% of the theoretical amount of acid in the presence of acetate ion, to 1% of the theoretical amount of acid in the presence of 2,6-lutidine (Table XII). It is suggested that these titers as well as that of crotyl 2,6-dimethylben-

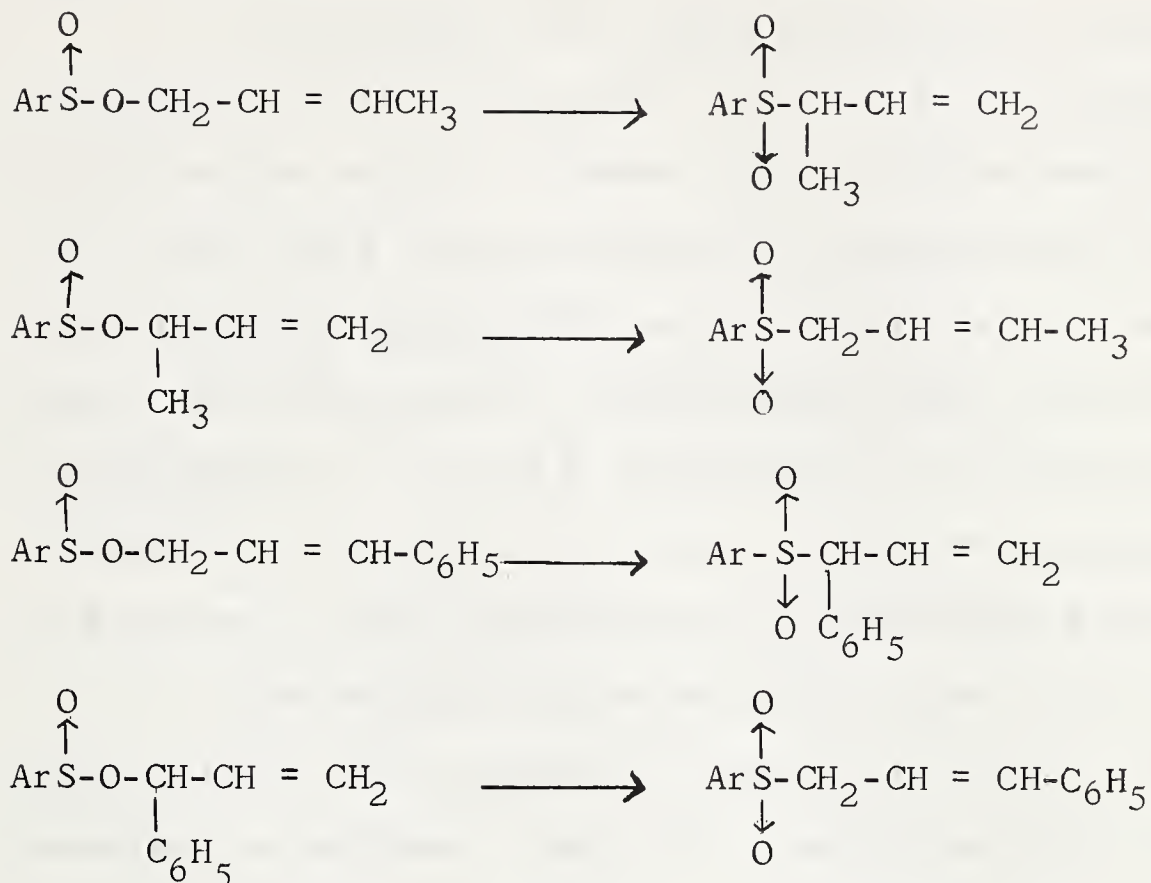
zenesulfinate in 60% ethanol-water with acetate ion present (3.5%, Table XII) may also be attributed to sulfur-oxygen bond fission.

Due to the higher rate of rearrangement of cinnamyl 2,6-dimethylbenzenesulfinate as compared with the allyl ester, even in anhydrous ethanol with sodium acetate present, only a small yield of ethyl 2,6-dimethylbenzenesulfinate was formed at 90.00°. With 2,6-lutidine present the rearrangement of this ester to sulfone was complete, as no ethyl 2,6-dimethylbenzenesulfinate could be detected and no acid was produced. The titer in 60% ethanol-water with acetate ion present (6.4%) is not by much higher than that with 2,6-lutidine present (5.8%) in this case. Accordingly, it is possible that the acid produced under these conditions may be due to either sulfur-oxygen, or carbon-oxygen bond fission or both. However, since in anhydrous ethanol with sodium acetate present, partial sulfur-oxygen bond fission was observed, at least part of the acid produced in 60% ethanol-water must be due to sulfur-oxygen bond fission.

B. Reaction mechanism.

The results obtained with the unsymmetrically substituted allylic 2,6-dimethylallylbenzenesulfonates (Table IX) indicate that the rearrangement of these esters to sulfones is accompanied by allylic rearrangement. Thus, crotyl and α -methylallyl 2,6-dimethylbenzenesulfonates rearranged to α -methylallyl and crotyl 2,6-dimethylphenyl sulfones, respectively. Similarly, cinnamyl and α -phenylallyl 2,6-dimethylbenzenesulfonates rearranged to α -phenylallyl and cinnamyl 2,6-dimethylphenyl

sulfones, respectively. These results are illustrated by the following equations.



In the case of crotyl, α -methylallyl and α -phenylallyl esters, apparently complete allylic rearrangement takes place during the sulfinic acid to sulfone isomerization. This seems to be also the case with the cinnamyl ester in acetonitrile.

At least 90% of the sulfone recovered from the reaction of cinnamyl 2,6-dimethylbenzenesulfinate in the run using 60% ethanol-water as solvent at 90.00° was α -phenylallyl 2,6-dimethylphenyl sulfone. The evidence for the presence of the cinnamyl 2,6-dimethylphenyl sulfone (ca. 10%) is based only on the fact that the infrared spectrum showed absorption at 960 cm^{-1} associated with trans. disubstituted olefinic double bonds and characteristic of this sulfone. However, any other compound

exhibiting these features might also have absorbed in the same region.

In agreement with these findings are the results of the stereospecific experiments, which have been carried out to determine the relation between the configurations of the optically active α, γ -dimethylallyl 2,6-dimethylphenyl sulfone and the corresponding optically active sulfinic acid from which it is produced. The inversion of configuration which occurs during the rearrangement of (+)- α, γ -dimethylallyl 2,6-dimethylbenzenesulfinic acid is consistent with the allylic rearrangement observed in the case of the unsymmetrically substituted allylic esters.

The evidence presented with regard to allylic rearrangement excludes the formation of dissociated ions as the principal precursor to sulfone, since such a mechanism would yield a mixture of two isomeric sulfones. In addition, the composition of the product mixture obtained from the α substituted allylic sulfinic acid would be expected to be similar to that obtained from the isomeric γ substituted allylic sulfinic acid. The observed data may be consistent with either an ion pair mechanism, or a more concerted cyclic intramolecular mechanism involving little change between the polarity of the ground state and transition state. It is interesting that even the cinnamyl ester undergoes allylic rearrangement, in spite of the loss of the resonance stabilization energy between the double bond and phenyl group, involved in this process.

In considering the substituent effect it may be pointed out that in general, the reaction rate of a system proceeding by

an ionization mechanism is expected to be accelerated by the substitution of an α hydrogen by an alkyl or aryl group. This acceleration in rate is a result of the stabilization provided by the alkyl or aryl group to the intermediate carbonium ion, due to inductive and resonance effects. In the case of allylic compounds and in the absence of interfering factors, the substituent effect in the γ position should be roughly the same as that in the α position, due to the resonance structure of the allylic carbonium ion.

The relative rates of rearrangement of the various allylic 2,6-dimethylbenzenesulfonates in 60% ethanol-water at 90.00° (Table XIX) are indicative of a polar transition state of reaction. The order of reactivity of the esters is as follows: allyl < crotyl < α -methylallyl \sim cinnamyl < α, γ -dimethylallyl < α -phenylallyl. However, the magnitude of the substituent effect is much smaller than that observed with ionizing systems. To illustrate this point, a comparison is made with the relative rates of solvolysis of allylic chlorides in 99.5% formic acid at 44.6° (8), which are also shown in Table XIX. It is found that in the case of allylic chlorides, the effect of a methyl group in the γ position is larger by two powers of ten and in the α position by one power of ten than in the case of allylic 2,6-dimethylbenzenesulfonates. The effect of two methyl groups, one in each α and γ positions, is larger by five powers of ten in the case of the allylic chlorides. Similarly, the effect of a phenyl group in the γ position of allyl chloride is three powers of ten larger, and in the α position five powers of ten larger, as com-

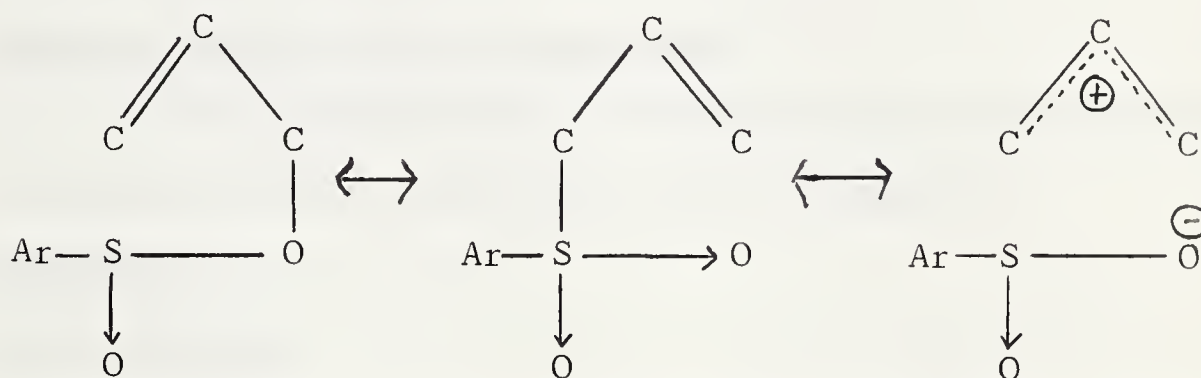
pared to allyl 2,6-dimethylbenzenesulfinate. The large difference in sensitivity to substituent effects between the allylic chlorides and 2,6-dimethylbenzenesulfonates tends to exclude a completely ionic mechanism for the rearrangement of sulfonates to sulfones.

The substituent effect data related to the rearrangement of the allylic 2,6-dimethylbenzenesulfonates, compares favourably with the corresponding data reported by Illiceto(4b) for the rearrangement of allylic thiocyanates to isothiocyanates in acetonitrile at 60°, and by Smith(5) for the rearrangement of allylic thionbenzoates to thiolbenzoates in the same solvent at 100°. The rearrangement of the last two systems is believed to involve little change in charge separation between the ground state and transition state (4b, 5). It is suggested that the same would apply for the rearrangement of allylic 2,6-dimethylbenzenesulfonates to sulfones as well.

Examination of the data in Table XX shows that the entropies of activation (ΔS^\ddagger) for the rearrangement of allyl, crotyl, α -methylallyl, cinnamyl and α,δ -dimethylallyl 2,6-dimethylbenzenesulfonates in 60% ethanol-water and that of α -phenylallyl 2,6-dimethylbenzenesulfonate in cyclohexane, all have negative values, ranging between -8.1 and -21.9 e.u. This would tend to support a highly ordered transition state consistent with a cyclic mechanism for the rearrangement of sulfonate to sulfone. Negative entropies of activation have been obtained for the rearrangement of other allylic systems which show very low sensitivity to solvent and substituent effects. For example, Smith

and Emerson(4a) have reported an entropy of activation of -9 e.u. for the isomerization of allyl thiocyanate in toluene, and Gagneaux, Winstein and Young(20) have reported average entropies of activation of -10 e.u. and -11 e.u. for the isomerization of α,α -dimethylallyl and δ,δ -dimethylallyl azide, respectively, in pentane, ether and 70% acetone.

On the basis of the evidence presented in this and preceding chapters, it is suggested that the rearrangement of the allylic 2,6-dimethylbenzenesulfonates to corresponding sulfones, proceeds by a cyclic intramolecular mechanism involving a transition state of the form shown below:



Further evidence for the importance of both ionic and covalent resonance structures of the transition state, is presented in Chapter 3.

EXPERIMENTAL

Solvents

Acetonitrile.

Fisher certified reagent grade acetonitrile was purified according to the method described by Smith, Fainberg and Winstein(18). The solvent which was first distilled from phosphorous pentoxide, was refluxed over anhydrous potassium carbonate for a few hours and then redistilled from phosphorous pentoxide, b.p. 78-79°, n_D^{25} 1.3420 (reported(18) n_D^{25} 1.3420). The solvent contained less than 0.001% water, as determined by a Karl Fischer titration.

Ethanol, acetic acid, cyclohexane.

The purification of these solvents and the preparation of aqueous ethanol were described in Chapter 1.

Materials

Allyl Alcohol.

Fisher reagent grade allyl alcohol was fractionally distilled, and the fraction boiling at 92-94° was collected, n_D^{25} 1.4113 (reported(43) b.p. 96-97°, n_D^{20} 1.41345).

Crotyl alcohol.

Lithium aluminum hydride (15.2 g., 0.4 mole) was added to 800 ml. of anhydrous diethyl ether in a three liter three-necked flask provided with a condenser, stirrer and a dropping funnel, and protected from atmospheric moisture with calcium chloride drying tubes. Freshly distilled crotonaldehyde, b.p. 97° (56 g., 0.8 mole), dissolved in 100 ml. of anhydrous ether, was added dropwise with stirring, such that the ether refluxed

gently. When the addition of the crotonaldehyde solution was completed, the reaction mixture was cooled in an ice-water bath and 15 ml. of water, 15 ml. of 15% NaOH, and 45 ml. of water were added in succession with continuous stirring. The appearance of a white precipitate was observed. The precipitate was filtered with suction and washed twice with ether, ethereal washings being combined with the filtrate. The ether solution was then washed once with water, and after drying over anhydrous magnesium sulfate, the solvent was removed by distillation through a Vigreux column. The crotyl alcohol was obtained by fractional distillation of the residue, and collecting the fraction boiling at 115-117°. Yield, 31 g. (55%), n_D^{25} 1.4238 (reported (43) b.p. 118°, n_D^{20} 1.4240). This compound showed a strong band in the infrared at 962 cm^{-1} (CS_2).

α -Methylallyl alcohol.

A 48.6 g. quantity (2 moles) of magnesium turnings was placed in a three liter three-necked flask equipped with a stirrer, condenser, and a dropping funnel. Iodomethane (282 g., 2 moles), dissolved in 700 ml. of anhydrous ether was added gradually with stirring and cooling in an ice-water bath. The cooling bath was then removed, and the reaction mixture was gently refluxed on a steam bath for one hour. Freshly distilled acrolein, b.p. 50-52° (112 g., 2 moles) dissolved in 300 ml. of anhydrous ether, was added slowly with stirring and cooling in an ice-water bath. This was followed by the addition of 300 ml. of saturated ammonium chloride solution, gradually and with continuous stirring and cooling. The ether solution was decanted

from the precipitate. The precipitate was washed with ether and washings combined with the ether solution. The solvent was removed by distillation through a Vigreux column and the residue fractionally distilled, using the same column. The fraction distilling at 92-94° was collected (reported(43) b.p. 96-97°). Yield 25 g. (17%) n_D^{25} 1.4092 (reported(44) n_D^{25} 1.4110)

Cinnamyl alcohol.

Eastman 'white label' grade cinnamyl alcohol was used without further purification. The compound was solid at room temperature and had n_D^{25} 1.5800 after melting (reported(43) m.p. 33°, n_D^{20} 1.5819). The alcohol showed strong absorption in the infrared at 963 cm^{-1} .

α -Phenylallyl alcohol.

Magnesium turnings (41.5 g., 1.7 mole) was placed in a three liter three-necked flask equipped with a stirrer, condenser, and a dropping funnel. The flask was placed in an ice-water bath, and bromobenzene (266.9 g., 1.7 mole) dissolved in one liter of anhydrous ether, was added dropwise with stirring. When the addition of the bromobenzene solution was completed, the reaction mixture was gently refluxed for one hour, after which the mixture was cooled again, and freshly distilled acrolein, b.p. 50-52° (97 g., 1.73 mole), dissolved in 300 ml. of anhydrous ether, was added gradually with stirring. A 300 ml. quantity of saturated ammonium chloride solution was added slowly with stirring and cooling. The formation of a white precipitate was observed. The ether solution was decanted to another flask and precipitate washed twice with ether. The ethereal

washings were added to the ether solution, and solvent evaporated using a water pump. The alcohol was obtained by distillation under reduced pressure. Yield, 144 g. (63.2%), b.p. 110-114°/22-25 mm., n_D^{25} 1.5401 (reported(45) yield 72%, b.p. 91.5°/5 mm., n_D^{25} 1.5390).

All alcohols were stored in dark bottles in the refrigerator.

Allyl 2,6-dimethylbenzenesulfinate.

To a 6.3 g. quantity (0.033 mole) of 2,6-dimethylbenzenesulfinyl chloride, dissolved in 30 ml. of Karl Fischer reagent grade pyridine and cooled in a dry ice-acetone bath, was added slowly 1.9 g. (0.030 mole) of allyl alcohol dissolved in 10 ml. of pyridine. The reaction mixture with the cooling bath was transferred to the refrigerator and left there overnight. The work-up procedure was as described for the preparation of α,γ -dimethylallyl 2,6-dimethylbenzenesulfinate (Chapter 1). Allyl 2,6-dimethylbenzenesulfinate, a liquid, had n_D^{25} 1.5470, infrared (CS_2): 770(s), 930, 970(s), 1140(s) cm^{-1} . The n.m.r. data are given in Table XI.

Analysis. Calculated for $C_{11}H_{14}O_2S$: C, 62.82; H, 6.71; S, 15.25. Found: C, 62.58, 62.64; H, 6.81, 6.58; S, 15.41.

The ester was stored in the refrigerator in pentane solution over anhydrous potassium carbonate.

Crotyl 2,6-dimethylbenzenesulfinate.

2,6 -Dimethylbenzenesulfinyl chloride (5.0 g., 0.027 mole) dissolved in Karl Fischer reagent grade pyridine (30 ml.) and cooled in a dry ice-acetone bath, was treated with a solution

of 2.0 g. (0.028 mole) of crotyl alcohol in 10 ml. of pyridine. After standing in the refrigerator overnight, the reaction mixture was worked up by the procedure employed with the corresponding α,γ -dimethylallyl ester (Chapter 1). Crotyl 2,6-dimethylbenzenesulfinate had n_D^{25} 1.5442, infrared (CS_2): 770(s), 900, 940(s), 960(s), 1135(s) cm^{-1} . The n.m.r. data are reported in Table XI.

Analysis. Calculated for $\text{C}_{12}\text{H}_{16}\text{O}_2\text{S}$: C, 64.25; H, 7.19; S, 14.29. Found: C, 64.11, 63.98; H, 7.30, 7.21; S, 14.18.

The ester was stored in the refrigerator in pentane solution over anhydrous potassium carbonate.

α -Methylallyl 2,6-dimethylbenzenesulfinate.

To a solution of 6.0 g. (0.032 mole) of 2,6-dimethylbenzenesulfinyl chloride in 30 ml. of Karl Fischer reagent grade pyridine which was cooled in a dry ice-acetone bath, was added slowly 2.4 g. (0.033 mole) of α -methylallyl alcohol dissolved in 10 ml. of pyridine. After standing in the refrigerator overnight, the reaction mixture was worked up by the procedure employed for the α,γ -dimethylallyl ester (Chapter 1). α -Methylallyl 2,6-dimethylbenzenesulfinate had n_D^{25} 1.5370, infrared(CS_2): 770(s), 835, 895, 920, 982, 1050, 1140(s). The n.m.r. data are presented in Table XI. The ester was stored in the refrigerator, in pentane solution over anhydrous potassium carbonate.

Cinnamyl 2,6-dimethylbenzenesulfinate.

A solution of 4.3 g. (0.032 mole) of cinnamyl alcohol in 10 ml. of Karl Fischer reagent grade pyridine, was added gradually to a solution of 6.2 g. (0.033 mole) of 2,6-dimethylbenzenesulfinyl chloride in 30 ml. of pyridine which was cooled in a dry

ice-acetone bath. The reaction mixture and cooling bath were transferred to the refrigerator and left there overnight. The work-up procedure of the mixture was the same as that described for the α,δ -dimethylallyl ester (Chapter 1).

The compound was crystallized from pentane, m.p. 39.8-41.0° infrared (CS₂): 690(s), 712, 725, 755, 770(s), 830, 945(s), 960(s), 1135(s) cm⁻¹. The n.m.r. data are given in Table XI.

Analysis. Calculated for C₁₇H₁₈O₂S: C, 71.29; H, 6.35; S, 11.19. Found: C, 71.44, 71.26; H, 6.28, 6.17; S, 11.07.

The ester was stored in the refrigerator.

α -Phenylallyl 2,6-dimethylbenzenesulfinate.

To a solution of 4.3 g. (0.023 mole) of 2,6-dimethylbenzenesulfinyl chloride in 10 ml. of Karl Fischer reagent grade pyridine, cooled in a dry ice-acetone bath, was added gradually a cold solution of 3.0 g. (0.022 mole) of α -phenylallyl alcohol in 2 ml. of pyridine. The reaction mixture and cooling bath were transferred to the refrigerator. After one hour, the mixture was poured into a mixture of ice and 10 ml. of concentrated hydrochloric acid, extracted with 200 ml. of ether and ether layer washed successively with water, 10% sodium carbonate solution and water. This ester was very unstable at room temperature, and was therefore stored in the freezer compartment in ether or pentane solution over anhydrous potassium carbonate. n_D^{25} 1.5795, infrared (CS₂): 690(s), 730, 770(s), 925, 970, 1140(s). The n.m.r. data are reported in Table XI.

Product Analysis

The procedure for the product analysis runs (Table IX)

of allyl, crotyl and α -methylallyl 2,6-dimethylbenzenesulfonates was the same as that employed for the corresponding α,δ -dimethylallyl ester (Chapter 1). The product analysis run of cinnamyl 2,6-dimethylbenzenesulfonate in acetic acid was also carried out by the same procedure.

In the product run of cinnamyl 2,6-dimethylbenzenesulfonate in acetonitrile at 90.00° the reaction mixture was extracted with 60% ether-methylene chloride instead of ether. The product runs of cinnamyl and α -phenylallyl 2,6-dimethylbenzenesulfonates in 60% ethanol-water are described below.

A 0.248 g. quantity (0.000867 mole) of cinnamyl 2,6-dimethylbenzenesulfonate and a 0.245 g. quantity (0.00229 mole) of 2,6-lutidine were weighed into a 50 ml. volumetric flask and 60% ethanol-water solvent was added to the mark. After mixing, the solution was transferred to another flask, sealed and heated for two hours in the 90.00 \pm 0.03° constant temperature oil bath. After quenching in ice-water, the flask was cooled in the refrigerator overnight. A 0.185 g. quantity (75%) of α -phenylallyl 2,6-dimethylphenyl sulfone crystallized from the solution and was separated by filtration with suction. Extraction of the mother liquor with ether in the usual manner, gave another 0.035 g. (14%, based on starting material) of material, the infrared spectrum of which showed sulfone (1320 cm^{-1} in CS_2) and traces of alcohol (3600 cm^{-1}). On addition of pentane to the residue and cooling, some of the sulfone (0.022 g., 9%) crystallized from the solution. Its infrared spectrum (CS_2) showed olefinic absorption at 925, 960 and 980 cm^{-1} , indicative for the presence of both the

cinnamyl and α -phenylallyl allylic isomers. The infrared spectrum of the pentane soluble material showed sulfone and alcohol.

In the run using α -phenylallyl 2,6-dimethylbenzenesulfinate, a 0.465 g. quantity (0.00163 mole) of this ester and 0.299 g. (0.00364 mole) of anhydrous sodium acetate were weighed in a 50 ml. volumetric flask and 60% ethanol-water was added to the mark. After mixing, the stoppered flask was kept for 20 hours in the $25.00 \pm 0.01^\circ$ constant temperature water bath. A 0.288 g. quantity (62%) of cinnamyl 2,6-dimethylphenyl sulfone crystallized from the solution and was separated by filtration with suction. The mother liquor was then extracted with ether in the usual manner, to yield 0.116 g. (25% based on starting material) of material. On addition of pentane to this residue, more sulfone crystallized from the solution. The infrared spectrum (CS_2) of the pentane soluble portion (0.043 g., 9%) indicated the presence of sulfone and alcohol.

The physical properties of the allyl, crotyl, α -methylallyl, cinnamyl and α -phenylallyl 2,6-dimethylphenyl sulfones are summarized in Tables XI and XXI.

2,6-Dimethylthiophenol

This material was prepared according to the method described by Tarbel(46) for the preparation of m-thiocresol. Starting with 35 g. (0.3 mole) of 2,6-dimethylaniline, 6.5 g. (16%) of 2,6-dimethylthiophenol was obtained, b.p. $74-75^\circ/6$ mm., n_D^{25} 1.5687. The n.m.r. spectrum (CCl_4) showed three singlets at 3.1, 7.0 and 7.7 τ , assigned to the aromatic, thiol and orthomethyl protons, respectively; the found integrated ratio of the corresponding protons was 3:1.1:6.

TABLE XXI

A summary of properties and analyses of various allylic

2,6-dimethylphenyl sulfones.

Sulfone	M.p., °C	Infrared absorption ^a , cm ⁻¹	Formula	Carbon		Hydrogen		Sulfur	
				Calc.	Found	Calc.	Found	Calc.	Found
Allyl	42.4-43.2	1120, 1150, 1320	C ₁₁ H ₁₄ O ₂ S	62.82	62.71 62.64	6.71	6.44 6.57	15.25	15.34
Crotyl	--- ^b	1120, 1150, 1320	C ₁₂ H ₁₆ O ₂ S						
α-Methylallyl	59.0-60.2	1120, 1150, 1315	C ₁₂ H ₁₆ O ₂ S	64.25	64.41 64.10	7.19	7.01 6.88	14.29	14.18
Cinnamyl	140.5-140.8	1120, 1150, 1320	C ₁₇ H ₁₈ O ₂ S	71.29	71.55 71.63	6.35	6.56 6.51	11.19	11.10
α-Phenylallyl	130.8-131.4	1120, 1145, 1315	C ₁₇ H ₁₈ O ₂ S	71.29	71.22 71.33	6.35	6.12 6.02	11.19	11.15

a - Infrared spectra were taken in carbon disulfide. The values listed are those characteristic of the sulfonyl group. The ethylenic absorptions are listed in Table X.

b - This sulfone could not be crystallized ($n_D^{25} = 1.5466$).

p-Toluenesulfonylhydrazine.

A mixture of 20 g. (0.625 mole) of hydrazine and 20 g. of water was placed in a one liter three-necked flask, equipped with a condenser, stirrer and a dropping funnel. A solution of 45 g. (0.237 mole) of recrystallized p-toluenesulfonyl chloride (m.p. 68-69°) in 315 ml. of benzene, was added dropwise over a period of four hours, the temperature being maintained at 40-50°. The crystalline product was filtered with suction, washed with water and air-dried. Yield 40 g. (90.8%), m.p. 109-111° (reported(47) m.p. 112°).

(+)-2-Pentanol.

(+)- α,δ -Dimethylallyl acid phthalate (4.7 g., 0.02 mole), $[\alpha]_D^{25} +23.34^\circ$ ($\underline{1} = 1$, $\underline{c} = 5$, CHCl_3), was placed in a 500 ml. three-necked flask provided with a thermometer, condenser, and a gas inlet tube. Diethylene glycol dimethyl ether (diglyme, 230 ml.) and p-toluenesulfonylhydrazine (7.6 g., 0.04 mole) were added, and the mixture heated for two hours at ca. 150° under a slow stream of nitrogen(38). After cooling, the solution was poured over crushed ice and extracted with 500 ml. of ether. The ether solution was washed several times with water, then with dilute hydrochloric acid solution and again with water. The acid phthalate was extracted from the ether solution with 200 ml. of 5% aqueous sodium carbonate. The carbonate extract was acidified with dilute hydrochloric acid and then extracted with ether. The ether layer was washed with water and dried over anhydrous magnesium sulfate. Evaporation of the solvent, using a water aspirator, gave 3 g. (64%) of (+)-2-pentyl acid phthalate, $[\alpha]_D^{25} +25.58^\circ$

(1 = 1, c = 5, CHCl₃), (reported(37) $[\alpha]_D^{25} +36.94^\circ$ (c = 5, CHCl₃)); infrared (CS₂): 750(s), 1070, 1110, 1280(s), strong doublet at 1690 and 1720 cm⁻¹.

(+)-2-Pentyl acid phthalate (3 g. 0.013 mole) was placed in a 100 ml. round bottom flask provided with a condenser, and 5 ml. of 8N sodium hydroxide solution was added. The mixture was heated for 10 minutes on a steam bath. After cooling it was extracted with 100 ml. of pentane. The pentane extract was washed with water, dried over anhydrous magnesium sulfate, and the solvent was removed by distillation through a Vigreux column to yield 1.7 g. of impure alcohol (theoretical yield, 1.15 g.), n_D^{25} 1.4050 (reported for racemic 2-pentanol(43) n_D^{20} 1.4053), infrared (CS₂): 3615 cm⁻¹, $[\alpha]_D^{25} +5.42^\circ$ (1 = 1, c = 5, CHCl₃) (reported(37) $[\alpha]_D^{25} +13.86^\circ$).

(+)-2-Pentyl p-toluenesulfonate (48).

(+)-2-Pentanol (1.3 g., 0.015 mole) was dissolved in 12 ml. of Karl Fischer grade pyridine and the solution cooled to -5° in an ice-salt bath. p-Toluenesulfonyl chloride (2.8 g., 0.015 mole) was added and the suspension gently swirled in the cooling bath until all the TsCl dissolved. After keeping at 0° for two and one half hours, one milliliter of water was added with cooling and swirling. The solution was then diluted with 10 ml. of water and extracted with three 10 ml. portions of chloroform. The combined chloroform extracts were washed successively with cold dilute sulfuric acid, water and sodium bicarbonate solution. After drying over sodium sulfate, and evaporation of the solvent under low pressure, 1.2 g. of (+)-2-pentyl

p-toluenesulfonate was obtained, n_D^{25} 1.4972. The compound showed strong absorption in the infrared at 895, 1172, and 1185 (doublet) and 1365 cm^{-1} (CS_2). $[\alpha]_D^{25} +4.38^\circ$ ($\underline{1} = 1$, $\underline{c} = 5$, CHCl_3). The racemic 2-pentyl p-toluenesulfonate, prepared by the same method, had n_D^{25} 1.4992 (reported(49) n_D^{25} 1.5005) and showed similar infrared absorption in CS_2 .

(+)-2-Pentyl 2,6-dimethylphenyl sulfide.

(+)-2-Pentyl p-toluenesulfonate (0.5 g., 0.0022 mole) was treated with 5 ml. of ethanolic 1 N sodium 2,6-dimethylthiophenoxide, and the mixture was left for 44 hours at room temperature. A 10 ml. quantity of 1 N sodium hydroxide was then added, the product extracted with 100 ml. pentane and pentane extract washed with water and dried over anhydrous potassium carbonate. Evaporation of the solvent gave 0.383 g. (92%) of (+)-2-pentyl 2,6-dimethylphenyl sulfide, n_D^{25} 1.5440, $[\alpha]_D^{25} +1.25^\circ$ ($\underline{1} = 1$, $\underline{c} = 19.15$, CHCl_3).

(+)-2-Pentyl 2,6-dimethylphenyl sulfone.

To 0.383 g. (0.0019 mole) of (+)-2-pentyl 2,6-dimethylphenyl sulfide, placed in a 100 ml. round bottom flask provided with a condenser, were added 10 ml. of dry acetic acid and ten drops of 30% H_2O_2 . The mixture was allowed to stand for 20 hours at room temperature after which it was heated on a steam bath for ten minutes. After cooling, 100 ml. of pentane-ether was added, solution washed with water and 10% aqueous sodium carbonate, and dried over anhydrous potassium carbonate. Evaporation of the solvent using a water aspirator, gave 0.290 g. (63%) of (+)-2-pentyl 2,6-dimethylphenyl sulfone, m.p. $37-40^\circ$ (from pentane-ether),

$[\alpha]_D^{25} +22.0^\circ$ ($\underline{1} = 1$, $\underline{c} = 2.5$, CHCl_3). Infrared (CS_2): 770(s), 1120(s), 1145(s), 1312(s) cm^{-1} .

Reduction of (+)- α, δ -dimethylallyl 2,6-dimethylphenyl sulfone.

A mixture of (+)- α, δ -dimethylallyl 2,6-dimethylphenyl sulfone ($[\alpha]_D^{25} +7.02^\circ$ ($\underline{1} = 1$, $\underline{c} = 4.9$, CHCl_3), 0.157 g., 0.66 mmole), *p*-toluenesulfonylhydrazine (0.380 g., 2 mmole), and ethylene glycol (20 ml.) was placed in a 500 ml. three-necked flask equipped with a condenser, a thermometer and a gas inlet tube. The mixture was heated for one hour at 150° under a slow stream of nitrogen, and after cooling poured over crushed ice. The product was extracted with 200 ml. of ether, washed successively with water, 10% hydrochloric acid, 10% aqueous sodium carbonate and water, and then dried over anhydrous potassium carbonate. Evaporation of the solvent using a water aspirator gave 0.160 g. of (+)-2-pentyl 2,6-dimethylphenyl sulfone which after crystallization from pentane had $[\alpha]_D^{25} +22.6^\circ$ ($\underline{1} = 1$, $\underline{c} = 0.5$, CHCl_3). Infrared (CS_2): 770(s), 1120, 1145(s), 1312(s) cm^{-1} . The sulfone obtained from another reduction on the same scale had $[\alpha]_D^{25} +20.2^\circ$ ($\underline{1} = 1$, $\underline{c} = 2.1$, CHCl_3).

Kinetic measurements.

The procedure for preparation of the solutions was as described in Chapter 1. The runs at 70° and 90° were carried out in oil baths thermostated at $70.07 \pm 0.02^\circ$ and $90.00 \pm 0.03^\circ$, respectively. The sealed ampoule technique was used for these runs. The runs at 25° were carried out in a water bath thermostated at $25.00 \pm 0.01^\circ$. In these runs, the samples were trans-

ferred directly from the thermostated flask to the extraction solvent at recorded intervals. The volume of sample extracted was 5 ml. in each case. Except for the runs of α -phenylallyl ester, the extraction solvent used was pentane. In the run of α -phenylallyl 2,6-dimethylbenzenesulfinate using acetonitrile as solvent, the samples were extracted with 60% ether-methylene chloride, while in the other runs of this ester, ether was used for extraction. Each sample was extracted with 25 ml. of solvent, washed with five 10 ml. portions of distilled water, shaking the mixture 50 times for each washing, and extract dried over anhydrous potassium carbonate. After evaporation of the solvent using a water aspirator, the residue was dissolved in one ml. of Eastman spectrograde bromoform, measured with an automatic pipette. This solution was transferred to a 0.5 mm. sodium chloride cell, previously balanced with a reference cell of the variable type, and the infrared spectrum in the regions specified below determined on a Perkin Elmer Infrared Spectrophotometer Model 21, using the 20 cm./micron scale.

<u>2,6-Dimethylbenzene sulfinate</u>	<u>IR region scanned, microns</u>	<u>IR band measured, microns</u>
Allyl	9.9 - 11.5	10.35
Crotyl	10.0 - 11.8	11.15
α -Methylallyl	11.5 - 12.6	12.04
Cinnamyl	11.5 - 12.4	12.03
α -Phenylallyl	10.5 - 11.6	10.80

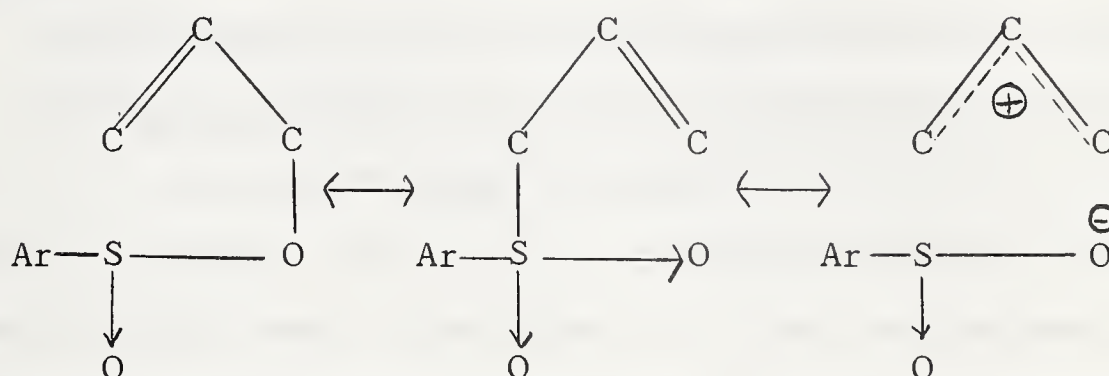
Lambert-Beer law and extraction procedure control runs.

These runs were carried out as described in Chapter 1.

CHAPTER 3

The Nature of the Transition State for the Rearrangement of Allylic 2,6-Dimethylbenzenesulfonates to Sulfones.

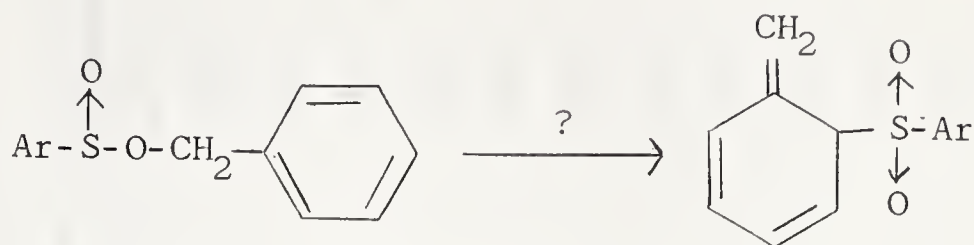
On the basis of the data described in the first two chapters, it was suggested that the rearrangement of the allylic 2,6-dimethylbenzenesulfonates to sulfones occurred by a cyclic intramolecular mechanism. It was also suggested that the transition state of this rearrangement might be represented by a resonance hybrid of the following resonance structures:



In order to gauge the importance of the ionic structure, the sensitivity of the rate of rearrangement of allyl and cinnamyl 2,6-dimethylbenzenesulfonates to solvent ionizing power was compared with that of *p*-methoxyneophyl *p*-toluenesulfonate. The reaction of various allylic 2,6-dimethylbenzenesulfonates in formic acid was also studied.

An examination was also made of the reaction of benzyl 2,6-dimethylbenzenesulfonate under the reaction conditions employed for the rearrangement of the corresponding allylic esters. This compound is not likely to yield sulfone of rearranged allylic structure, since the formation of such a product would require

the loss of the resonance stabilization energy associated with the benzene ring.



The results obtained from these investigations are presented in this chapter.

RESULTS

A. Determination of the solvent sensitivity for the rearrangement of cinnamyl and allyl 2,6-dimethylbenzenesulfonates.

In order to gage the sensitivity of rate of rearrangement of cinnamyl and allyl 2,6-dimethylbenzenesulfonates to solvent ionizing power, the kinetics of the rearrangement of these esters were determined in a number of hydroxylic and non-hydroxylic solvents. The solvents used for this purpose were selected from those employed by Smith, Fainberg and Winstein(18) for the solvolysis of *p*-methoxyneophyl *p*-toluenesulfonate. The results are reported in Tables XXII and XXIII for cinnamyl and allyl 2,6-dimethylbenzenesulfonates, respectively.

A product analysis run on the reaction of allyl 2,6-dimethylbenzenesulfonate in acetic acid was also carried out. A 50 ml. solution of the allyl ester (0.403 g. 0.00192 mole) in acetic acid with added 2,6-lutidine (0.0673 M) was heated on a steam bath for 46 hours. Extraction of the solution with ether gave 0.200 g. (49.6%) of allyl 2,6-dimethylphenyl sulfone, contaminated with acetate (infrared bands at 1740 and 1225 cm^{-1} , in CS_2).

TABLE XXII

Kinetic data for the rearrangement of cinnamyl 2,6-dimethyl-
benzenesulfinate to α -phenylallyl 2,6-dimethylphenyl sulfone.

at 90.00 \pm 0.03°

Run #	Solvent	(Ester), M	(Base), M	$10^4 k$, sec ⁻¹	Notebook ref.
40	60% EtOH-H ₂ O	0.0215	0.0500 ^a	10.1 \pm .60	162-1
49	50% Dioxane-H ₂ O	0.0193	0.0486 ^a	7.3 \pm .20	200-1
47	80% EtOH-H ₂ O	0.0206	0.0483 ^a	5.36 \pm .33	196-1
46	60% Dioxane-H ₂ O	0.0195	0.0439 ^a	4.15 \pm .13	195-1
41	AcOH	0.0213	0.0540 ^a	4.24 \pm .19	164-1
48	70% Dioxane-H ₂ O	0.0226	0.0505 ^a	2.19 \pm .12	197-1
42	EtOH	0.0201	0.0458 ^a	1.97 \pm .05	165-1
57	EtOH	0.0203	0.0609 ^b	1.73 \pm .03	240-1
50	80% Dioxane-H ₂ O	0.0224	0.0476 ^a	1.18 \pm .05	201-1
54	Me ₂ SO	0.0230	0.0488 ^b	0.766 \pm .045	217-1
51	MeCN	0.0224	0.0464 ^b	0.515 \pm .012	202-1
52	12.5% AcOH-Dioxane	0.0234	0.0448 ^b	0.364 \pm .015	203-1
53	(CH ₂) ₄ O	0.0231	0.0495 ^b	0.153 \pm .003	204-1

a - Sodium acetate.

b - 2,6-Lutidine.

TABLE XXIII

Kinetic data for the rearrangement of allyl 2,6-dimethylbenzene-sulfinate to allyl 2,6-dimethylphenyl sulfone at $90.00 \pm 0.03^\circ$.

Run #	Solvent	(Ester), M	(2,6-Lutidine), M	$10^6 k$, sec. ⁻¹	Notebook ref.
21	60% EtOH-H ₂ O	0.0218	0.0514	$4.57 \pm .20$	101-1
67	50% Dioxane-H ₂ O	0.0218	0.0550	$4.86 \pm .23$	38-2
66	80% EtOH-H ₂ O	0.0232	0.0468	$2.72 \pm .15$	37-2
65	60% Dioxane-H ₂ O	0.0281	0.0475	$4.12 \pm .12$	284-1
29	AcOH	0.0260	0.0516	$6.35 \pm .26$	130-1
68	70% Dioxane-H ₂ O	0.0222	0.0400	$2.44 \pm .04$	41-2
55	EtOH	0.0228	0.0439	$1.25 \pm .04$	36-2
69	80% Dioxane-H ₂ O	0.0207	0.0443	$1.70 \pm .08$	42-2
64	MeCN	0.0212	0.0488	$0.804 \pm .046$	283-1
63	12.5% AcOH-Dioxane	0.0240	0.0489	$0.737 \pm .013$	282-1
62	(CH ₂) ₄ O	0.0246	0.0421	$0.373 \pm .015$	280-1

B. The reaction of allylic 2,6-dimethylbenzenesulfinates in formic acid.

The reaction of various allylic 2,6-dimethylbenzenesulfinates in anhydrous formic acid with sodium formate present at 25.00°, was examined. Partial or complete solvolysis to yield formate esters occurred. The half-lives obtained by measuring the rate of ester disappearance using the infrared method previously described (Chapter 2), are given in Table XXIV.

TABLE XXIV

A summary of half-lives for the reaction of various allylic 2,6-dimethylbenzenesulfinates in formic acid at 25.00 ± 0.01°

2,6-Dimethyl benzenesulfinate	(Ester), M	(HCO ₂ Na), M	t _{1/2} , min.	Notebook ref.
Allyl	0.0406	0.0600	745	295-1
"	0.0208	0.3000	837	298-1
Crotyl	0.0230	0.0600	360	291-1
α-Methylallyl	0.0295	0.0500	420	6-2
Cinnamyl	0.0200	0.0500	ca. 3	287-1
"	0.0208	0.3000	22	290-1
α-Phenylallyl	0.0199	0.1000	≤ 0.5	3-2

In addition to the characteristic 2,6-dimethylbenzenesulfinate infrared absorption band recorded for kinetic measurements, the infrared regions of the formate ester band at 5.83 microns and sulfone and thiosulfonate band at 7.6-7.7 microns (in bromoform) were also recorded. Using this procedure, no sulfone was detected from the runs of allyl and crotyl 2,6-di-

methylbenzenesulfinates in formic acid (Table XXIV). However, in both runs as well as in that of α -methylallyl 2,6-dimethylbenzenesulfinate, 2,6-dimethylphenyl 2,6-dimethylbenzenethiosulfonate was produced as evidenced by an infrared absorption band at 7.60 microns. This product is probably formed from 2,6-dimethylbenzenesulfinic acid, on prolonged standing under acidic conditions.

Only traces of formate esters were detected in the infrared spectra of the samples obtained from the formolysis of allyl, crotyl and α -methylallyl 2,6-dimethylbenzenesulfinates. The formate esters were lost during the work-up procedure. This point was verified by a control run in which crotyl alcohol (0.0486 M) was treated with formic acid containing 0.0500 M sodium formate for 16 hours at 25.00°. No residue was obtained after extraction and evaporation of the solvent at the water aspirator.

However, the formate esters could be detected if the extraction solvent was removed by distillation through a Vigreux column at atmospheric pressure. In this way, definite infrared evidence could be obtained on the formation of formate ester(s) in a product run carried out on α -methylallyl 2,6-dimethylbenzenesulfinate (0.0610 M) in formic acid, containing 0.1000 M sodium formate and maintained at 25.00° for 150 hours. It is not known if the ester is α -methylallyl or crotyl formate or a mixture of both esters. On evaporation of the formate esters at the water aspirator and removal of the thiosulfonate by crystallization, a 27% yield of crotyl 2,6-dimethylphenyl sulfone was recovered in this run.

Unlike the formate esters of the lower molecular weight allylic alcohols, the cinnamyl formate formed from the reaction of cinnamyl 2,6-dimethylbenzenesulfinate is not affected during the product isolation procedure. Cinnamyl formate (strong infrared bands at 960, 1150 and 1725 cm^{-1} in CS_2) is the only allylic isomer formed; no contamination with α -phenylallyl formate was observed. A low yield of sulfone (ca. 15%) is also formed, consisting of a mixture of the two allylic isomers, the cinnamyl and α -phenylallyl 2,6-dimethylphenyl sulfones (infrared bands at 925, 960 and 980 cm^{-1} in CS_2).

In this case, control runs were performed to test the possibilities of sulfone solvolysis and isomerization, or sulfone formation from alcohol and 2,6-dimethylbenzenesulfinic acid, under the reaction conditions. α -Phenylallyl 2,6-dimethylphenyl sulfone (0.0185 M) in formic acid containing 0.0500 M sodium formate, underwent no change even after two hours at 25.00° . Similarly, a mixture of cinnamyl alcohol (0.0194 M) and 2,6-dimethylbenzenesulfinic acid (0.0212 M) in formic acid with 0.0500 M sodium formate present, which was maintained for one hour at 25.00° , gave cinnamyl formate as the only product. It should also be mentioned that the rate of esterification of cinnamyl alcohol in formic acid is similar to the rate of disappearance of the cinnamyl 2,6-dimethylbenzenesulfinate under the same conditions.

The reaction of α -phenylallyl 2,6-dimethylbenzenesulfinate in formic acid, results in the formation of cinnamyl formate and cinnamyl 2,6-dimethylphenyl sulfone. Approximately a 40% yield of sulfone is obtained as determined by infrared. A control

run to check whether or not the sulfone had been formed from alcohol and 2,6-dimethylbenzenesulfinic acid was carried out. Cinnamyl formate was the only product isolated from a solution of α -phenylallyl alcohol (0.0172 M) and 2,6-dimethylbenzenesulfinic acid (0.0207 M) in formic acid containing 0.1000 M sodium formate, which was extracted immediately after its preparation at 25°.

In the attempt to trap a possible carbonium ion intermediate, sodium azide was added to solutions of cinnamyl and α -phenylallyl 2,6-dimethylbenzenesulfonates in buffered formic acid. The infrared spectrum of an extract from a solution of α -phenylallyl 2,6-dimethylbenzenesulfonate (0.0231 M) in formic acid containing 0.500 M sodium formate and 0.1261 M sodium azide (8 minutes at 25°) showed a weak band at 2100 cm^{-1} (CCl_4) characteristic of organic azide (50). Similar results were obtained with a solution of cinnamyl 2,6-dimethylbenzenesulfonate (0.0245 M) in formic acid containing 0.1000 M sodium formate and 0.1623 M sodium azide, which was maintained for 35 minutes at 25.00°.

C. The synthesis and reaction of benzyl 2,6-dimethylbenzenesulfonate.

Benzyl 2,6-dimethylbenzenesulfonate was prepared by treatment of benzyl alcohol with 2,6-dimethylbenzenesulfonyl chloride in pyridine in a dry ice-acetone bath. In order to establish the type of bond cleavage which this ester would undergo under solvolytic conditions, the reaction in anhydrous ethanol was examined. Complete conversion to ethyl 2,6-dimethylbenzenesulfonate (strong bands at 770, 882, 1015 and 1132 cm^{-1} in CS_2)

was observed on a sample of a solution of benzyl 2,6-dimethylbenzenesulfinate (0.0205 M) in anhydrous ethanol containing 0.0400 M sodium acetate, which had been heated for 12 hours at 90.00°.

A control run on the adherence of the sulfinate ester absorption at 11.08 and 12.01 microns to the Lambert-Beer law and on the extraction procedure, was carried out as previously described for the allylic esters (Chapter 1). The results obtained (Fig. 12) show good linearity. Where ethyl 2,6-dimethylbenzenesulfinate (IR band at 11.38 microns in bromoform) is a reaction product, it is more convenient to use the weaker band at 12.01 microns, for kinetic measurements so as to avoid interference of the ethyl ester. A kinetic run on the reaction of benzyl 2,6-dimethylbenzenesulfinate (0.0229 M) in anhydrous ethanol with 2,6-lutidine present (0.0510 M) at 90.00° was performed. The reaction was very slow and had a rate constant of ca. $2 \times 10^{-7} \text{ sec}^{-1}$. There was infrared evidence for the formation of ethyl 2,6-dimethylbenzenesulfinate (11.38 microns in bromoform), but not for the formation of any sulfone.

The reaction of benzyl 2,6-dimethylbenzenesulfinate (0.0229 M) in acetic acid with 2,6-lutidine present (0.0577 M), 90.00° was also examined. The rate constant for ester disappearance was equal to $3.93 \times 10^{-6} \text{ sec}^{-1}$. A 25 ml. portion of the solution was heated for 149 hours at 90.00° and then extracted in the usual manner. The residue (0.095 g.) was dissolved in pentane and cooled. The crystalline material was separated and identified as 2,6-dimethylphenyl 2,6-dimethylbenzenethiosulfonate

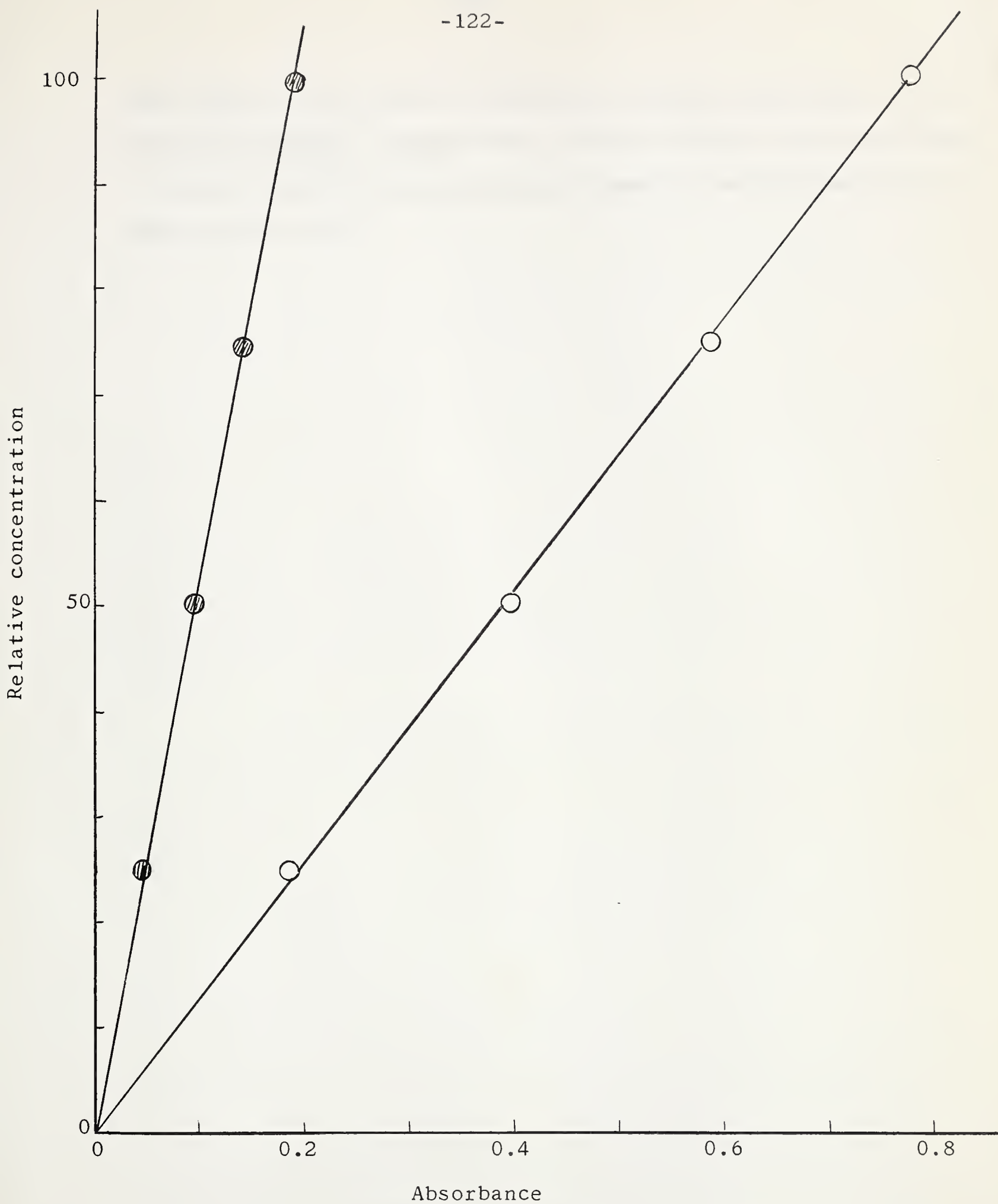


Fig. 12 - Lambert-Beer law and extraction procedure control for benzyl 2,6-dimethylbenzenesulfinate ($100 \equiv 0.0238$ M; ● at 12.01 microns, ○ at 11.08 microns).

(m.p. 121-123° and infrared spectrum identical with that of an authentic sample). The pentane soluble material was identified as benzyl acetate (strong infrared bands in carbon disulfide at 1220 and 1740 cm^{-1}).

DISCUSSION

A. Solvent sensitivity.

Smith, Fainberg and Winstein(18) have suggested the following equation to correlate the response of a reaction rate to solvent ionizing power with log k values for the ionization of p-methoxyneophyl p-toluenesulfonate:

$$\log k_{\text{reaction}} = \underline{a} \log k_1 + \underline{b}$$

where k_{reaction} and k_1 are the rate constants of the reaction being examined and that of ionization of p-methoxyneophyl p-toluenesulfonate, respectively. The a value in the above equation, which can be obtained graphically from a plot of $\log k_{\text{reaction}}$ versus $\log k_1$, was suggested by these authors as a measure of relative sensitivity of a reaction to the ionizing power of the solvent.

The rate constants for the rearrangement of cinnamyl and allyl 2,6-dimethylbenzenesulfonates at 90.00° reported in Tables XXII and XXIII, respectively, are summarized in Table XXV together with those reported by Smith, Fainberg and Winstein(18) for the ionization of p-methoxyneophyl p-toluenesulfonate. Examination of the data in Table XXV indicates that the change of rearrangement rate of allyl and cinnamyl 2,6-dimethylbenzenesulfonates with solvent ionizing power is smaller than that observed in the ionization of p-methoxyneophyl p-toluenesulfonate.

The log k values for the rearrangement of cinnamyl and allyl 2,6-dimethylbenzenesulfonates in the hydroxylic solvents (first eight solvents in Table XXV) at 90.00°, were correlated with the log k values for the ionization of p-methoxyneophyl

TABLE XXV

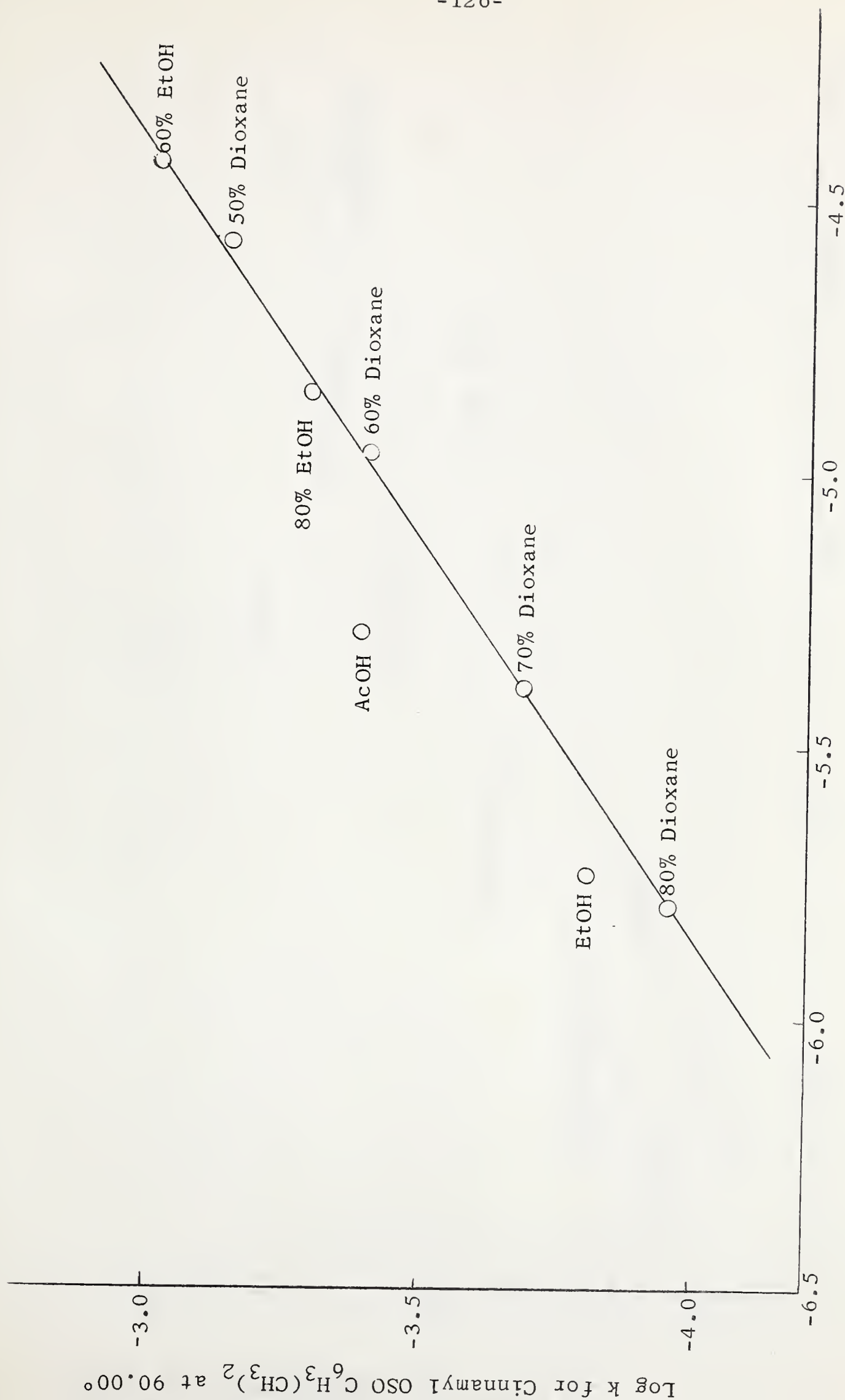
Rate constants for the rearrangement of cinnamyl and allyl 2,6-dimethylbenzenesulfonates and for the solvolysis of *p*-methoxyneophyl *p*-toluenesulfonate^a.

Solvent	Temp., °C.	Cinnamyl ^b 10 ⁴ k,sec ⁻¹	Allyl ^b 10 ⁶ k,sec ⁻¹	Temp., °C.	ROTs ^c 10 ⁵ k,sec ⁻¹
60% EtOH-H ₂ O	90	10.1	4.57	25	3.75
50% Dioxane-H ₂ O	90	7.3	4.86	25	2.66
80% EtOH-H ₂ O	90	5.36	2.72	25	1.41
60% Dioxane-H ₂ O	90	4.15	4.12	25	1.08
AcOH	90	4.24	6.35	25	0.54
70% Dioxane-H ₂ O	90	2.19	2.44	25	0.40
EtOH	90	1.73	1.25	25	0.18
80% Dioxane-H ₂ O	90	1.18	1.70	25	0.16
Me ₂ SO	90	0.766	-	75	18.2
MeCN	90	0.515	0.804	75	6.0
12.5% AcOH-Dioxane	90	0.364	0.737	75	1.21
(CH ₂) ₄ O	90	0.153	0.373	75	0.085

a - The data for the 2,6-dimethylbenzenesulfonates were extracted from Tables XXII and XXIII. The data for the *p*-methoxyneophyl *p*-toluenesulfonate were taken from Ref. 18.

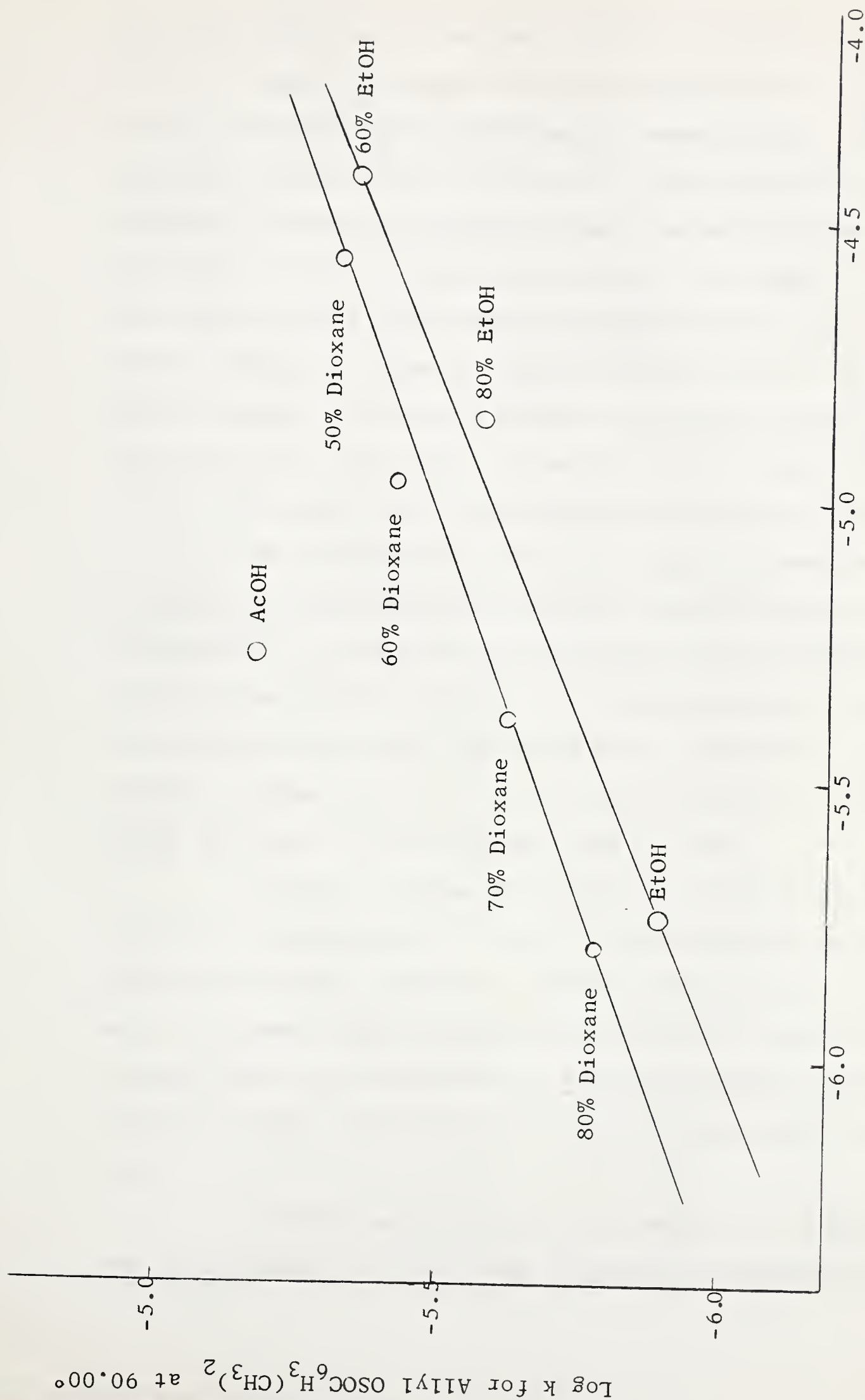
b - 2,6-Dimethylbenzenesulfinate.

c - *p*-Methoxyneophyl *p*-toluenesulfonate.



Log k for p-Methoxyneophyl OTs at 25.0°

Fig. 13 - Plot of log k for rearrangement of cinnamyl 2,6-dimethylbenzenesulfonate vs. log k for ionization of p-methoxyneophyl p-toluenesulfonate in hydroxylic solvents (slope = 0.68).



Log k for p-Methoxyneophyl OTs at 25.0°

Fig. 14 - Plot of log k for rearrangement of allyl 2,6-dimethylbenzenesulfonate vs. log k for ionization of p-methoxyneophyl p-toluenesulfonate in hydroxylic solvents.

p-toluenesulfonate in the same solvents at 25.0°. This is illustrated in Figs. 13 and 14 for the correlations of the cinnamyl and allyl 2,6-dimethylbenzenesulfonates, respectively. Judging from the good linearity shown in Fig. 13, the correlation for the cinnamyl 2,6-dimethylbenzenesulfonate is satisfactory. The slope (a value) of the straight line in Fig. 13 is equal to 0.68. In the case of allyl 2,6-dimethylbenzenesulfonate (Fig. 14), the points related to aqueous dioxane solution lie on one line, while those related to anhydrous ethanol and aqueous ethanol lie on a separate line, with slopes (a values) of 0.38 and 0.43, respectively. The acetic acid point deviates from both lines.

As illustrated in Fig. 15, log *k* for rearrangement of cinnamyl 2,6-dimethylbenzenesulfonate using dimethyl sulfoxide, acetonitrile, 12.5% acetic acid-dioxane and tetrahydrofuran as solvents (hereafter referred to as "non-hydroxylic") at 90.00°, is correlated quite well with log *k* for ionization of *p*-methoxyneophyl *p*-toluenesulfonate in the same solvents at 75.0°. The slope (a value) of the straight line is 0.30.

The plot in Fig. 16 shows good correlation between the log *k* for rearrangement of allyl 2,6-dimethylbenzenesulfonate in 80% ethanol-water, anhydrous ethanol, acetonitrile, 12.5% acetic acid - dioxane, and tetrahydrofuran at 90.00°, and the corresponding log *k* for ionization of *p*-methoxyneophyl *p*-toluenesulfonate at 75.0°. The slope (a value) for this plot is equal to 0.19.

From the magnitude of the a values it is clear that the rearrangement of allyl and cinnamyl 2,6-dimethylbenzenesul-

Log k for Cinnamyl OSOC₆H₃(CH₃)₂ at 90.00°

-4.0-

-4.5-

-5.0-

-129-

Me₂SO

O MeCN

12.5% AcOH-Dioxane

(CH₂)₄O

-6.0

-5.5

-5.0

-4.5

-4.0

Log k for p-Methoxyneophyl OTs at 75.0°

Fig. 15 - Plot of log k for rearrangement of cinnamyl 2,6-dimethylbenzenesulfonate vs. log k for ionization of p-methoxyneophyl p-toluenesulfonate in 'non-hydroxylic' solvents (slope = 0.30).

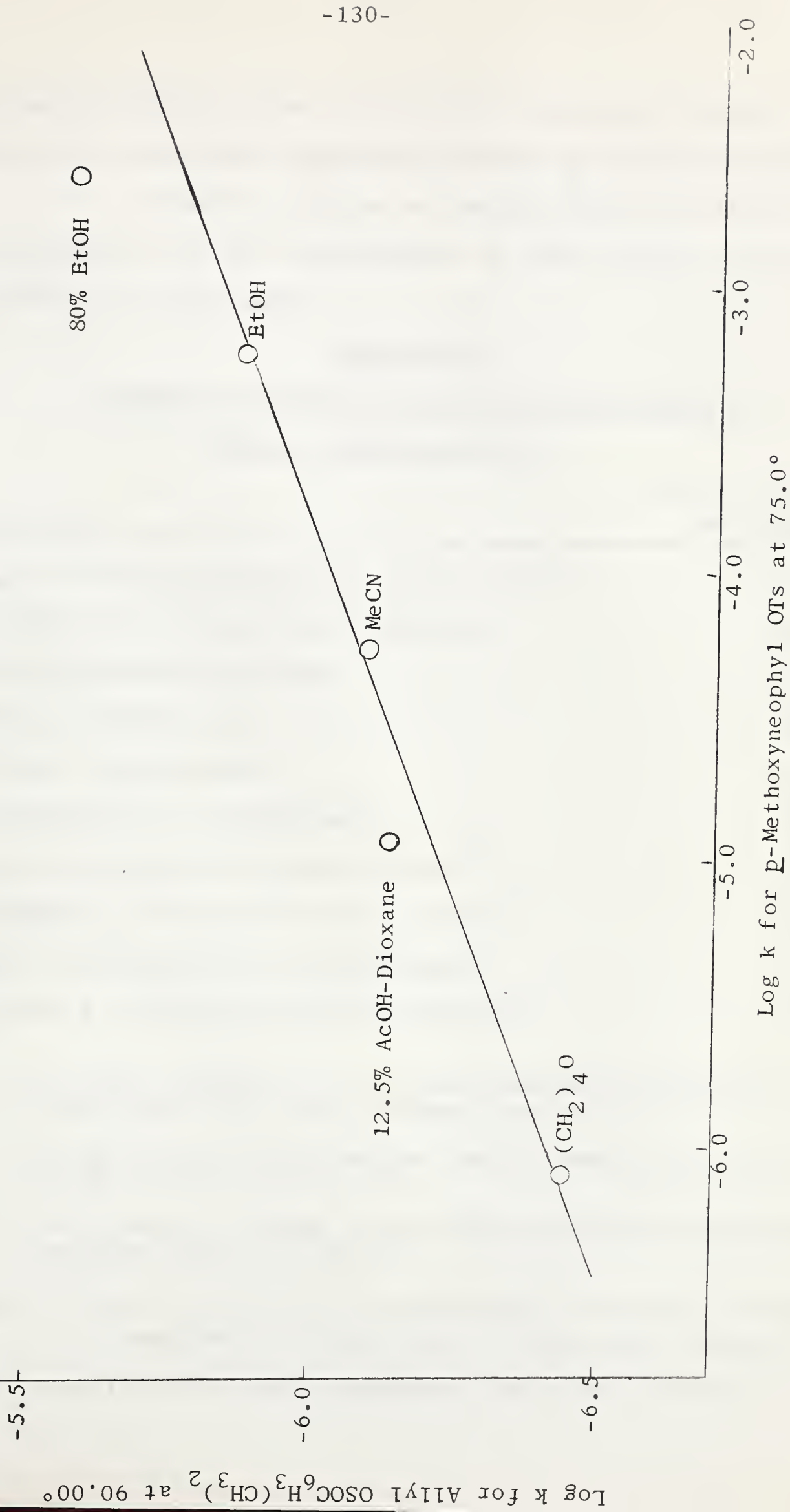


Fig. 16 - Plot of log k for rearrangement of allyl 2,6-dimethylbenzenesulfonate vs. log k for ionization of p-methoxyneophyl p-toluenesulfonate in "non-hydroxylic" solvents (slope = 0.19).

finates exhibit a lower sensitivity to solvent ionizing power than the ionization of *p*-methoxyneophyl *p*-toluenesulfonate.

It was of interest to compare the above data with data reported(5) for the rearrangement of other allylic systems. This is shown in Table XXVI.

TABLE XXVI

A summary of solvent sensitivities for several allylic rearrangements.^a

Compound	Solvent sensitivity parameter <u>a</u>
<u>cis</u> -5-Methyl-2-cyclohexenyl acid phthalate	0.94
1-Phenylallyl-3,4,5-tribromobenzoate	.57
α,α -Dimethylallyl azide	.12
Allyl thionbenzoate	.13
Crotyl thionbenzoate	.15
α -Methylallyl thionbenzoate	.13
Allyl 2,6-dimethylbenzenesulfinate ^b	.38
Cinnamyl 2,6-dimethylbenzenesulfinate ^b	.68
Allyl 2,6-dimethylbenzenesulfinate ^c	.19
Cinnamyl 2,6-dimethylbenzenesulfinate ^c	.30

a - All data, except for allyl and cinnamyl 2,6-dimethylbenzenesulfinate have been extracted from Ref. 5.

b - The a value is based on the correlation in hydroxylic solvents (Figs. 14 and 13).

c - The a value is based on the correlation in "non-hydroxylic" solvents (Figs. 16 and 15).

Examination of the data in Table XXVI indicates that the sensitivity of rearrangement of allyl and cinnamyl 2,6-dimethyl-

benzenesulfonates to solvent ionizing power is smaller than in the case of cis-5-methyl-2-cyclohexenyl acid phthalate, which has been interpreted to react by an ion-pair mechanism(51). In the "non-hydroxylic" solvents the rearrangement of the allylic 2,6-dimethylbenzenesulfonates exhibits a low sensitivity to variation in solvent ionizing power which is of the same order of magnitude as that observed for the rearrangement of allylic thionbenzoates and azides.

Assuming a polar transition state for the rearrangement of allylic 2,6-dimethylbenzenesulfonates, it may be anticipated that the substitution of an allylic hydrogen by a phenyl group would result in an increased sensitivity of reaction rate to solvent ionizing power. Accordingly, the larger ρ values observed for the rearrangement of cinnamyl 2,6-dimethylbenzenesulfonate as compared to those of the corresponding allyl ester are supporting evidence for the importance of an ionic resonance structure as a contributor to the resonance hybrid of the transition state (p.113).

B. Solvolysis and rearrangement in formic acid.

The interpretation of the results obtained from the experiments conducted in formic acid is less clear cut. Both acid catalyzed sulfur-oxygen and carbon-oxygen bond fission are likely to occur in this solvent. A consideration of the relative rates of reaction and the effect of change in sodium formate concentration on rate provide some information with regard to the type of bond fission which takes place.

The rate of reaction of cinnamyl 2,6-dimethylbenzene-

sulfinate in formic acid containing sodium formate is faster by a factor of two powers of ten than the rate of reaction of either crotyl or α -methylallyl 2,6-dimethylbenzenesulfinate under the same conditions (Table XXIV). This factor is similar to that observed by Vernon(8) for the solvolysis of the corresponding chlorides in 99.5% formic acid (Table XIX), and suggests that at least cinnamyl 2,6-dimethylbenzenesulfinate reacts by ionization.

The rate of reaction of α -phenylallyl 2,6-dimethylbenzenesulfinate in formic acid with added sodium formate, relative to that of the corresponding cinnamyl ester is also in the right direction for an ionization mechanism.

On the other hand, the rate of reaction of either crotyl or α -methylallyl 2,6-dimethylbenzenesulfinate in formic acid with sodium formate present, is only faster by a factor of two relative to that of the corresponding allyl ester instead by a factor of three powers of ten observed in the case of allylic chlorides (Table XIX). This result would indicate that in the case of allyl 2,6-dimethylbenzenesulfinate there is extensive sulfur-oxygen bond fission.

Some support to this conclusion is provided by the observed effect of increased sodium formate concentration on reaction rate. It may be anticipated that an increase of formate ion concentration would speed up the sulfur-oxygen bond fission, as a result of increase in nucleophile concentration, but at the same time it may slow it down as a result of a decrease in acid catalysis. For the acid catalyzed ionization, only the last effect would apply.

Reference to the data of Table XXIV indicates that when the sodium formate concentration was increased six fold, it caused a decrease in rate by a factor of ca. 7 in the case of cinnamyl 2,6-dimethylbenzenesulfinate. On the other hand, the rate of reaction of allyl 2,6-dimethylbenzenesulfinate decreased by only 12% when the sodium formate concentration was increased five fold. These results confirm the assumption with regard to acid catalysis by solvent, and are consistent with sulfur-oxygen bond fission in the case of allyl 2,6-dimethylbenzenesulfinate.

The formation of organic azide from the reaction of cinnamyl and α -phenylallyl 2,6-dimethylbenzenesulfonates in buffered formic acid with added sodium azide, is an indication of the presence of a carbonium ion intermediate.

In advance, the formation of sulfone in formic acid may be consistent with either sulfur-oxygen or carbon-oxygen bond fission. However, since no sulfone was produced by treatment of cinnamyl or α -phenylallyl alcohol with 2,6-dimethylbenzenesulfonic acid under the reaction conditions, the sulfone formed during the reaction of cinnamyl or α -phenylallyl 2,6-dimethylbenzenesulfonates in buffered formic acid could not be formed by sulfur-oxygen bond fission.

C. The reaction of benzyl 2,6-dimethylbenzenesulfinate

Benzyl 2,6-dimethylbenzenesulfinate in anhydrous ethanol at 90.00°, with either sodium acetate or 2,6-lutidine present, underwent sulfur-oxygen bond fission as evidenced by the formation of ethyl 2,6-dimethylbenzenesulfinate. No evidence for sulfone or ether could be detected by the infrared spectral data.

In anhydrous ethanol at 90.00° with added 2,6-lutidine, the rate of disappearance of benzyl 2,6-dimethylbenzenesulfinate by sulfur-oxygen bond fission was equal to ca. $2 \times 10^{-7} \text{ sec}^{-1}$. This rate constant must be higher than that of nucleophylic substitution by ethanol and still higher than that of ionization. Assuming that 10% of ethyl benzyl ether was formed, the rate constant for substitution by ethanol would be equal to ca. 2×10^{-8} .

This rate constant is between 2-12 times larger than that expected for the reaction of allyl 2,6-dimethylbenzenesulfinate under the same conditions, to yield the same yield of ethyl allyl ether. This estimate is based on the following considerations. The rate of ethanolysis of benzyl p-toluenesulfonate in ethanol at 25° is 12 times faster than that of the allyl p-toluenesulfonate under the same conditions (52). The rate of ethanolysis of benzyl chloride(53) in ethanol at 50.00° ($k = 3.14 \pm 0.06 \times 10^{-7} \text{ sec}^{-1}$) is some two times faster than that of allyl chloride(7) in ethanol at 44.6° ($k = 6.3 \times 10^{-8} \text{ sec}^{-1}$).

The rate constant for nucleophilic substitution by ethanol on allyl 2,6-dimethylbenzenesulfinate then, cannot be larger than 10^{-8} sec^{-1} . The product of this reaction would be the allyl ethyl ether. However, allyl 2,6-dimethylbenzenesulfinate in anhydrous ethanol with added 2,6-lutidine, rearranged to allyl 2,6-dimethylphenyl sulfone at a rate constant equal to $1.25 \times 10^{-6} \text{ sec}^{-1}$. By assuming that the rate of nucleophilic substitution by solvent should be only 10 times faster than that of ionization, it is found that the rate of rearrangement of allyl 2,6-dimethylbenzenesulfinate to the corresponding sulfone

is three powers of ten faster than estimated for an ionization process.

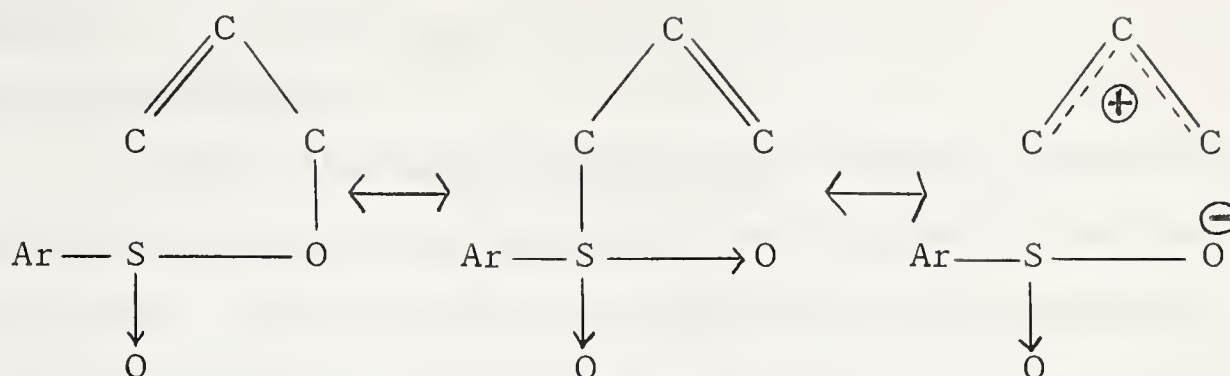
It is also possible to compare in a similar way, the data for α -methylallyl and α -phenylethyl 2,6-dimethylbenzenesulfonates on the basis of the available data for the corresponding chlorides.

The rate of ionization of α -phenylethyl chloride(54) in 50% ethanol-water at 50.0° ($k = 4.86 \times 10^{-3} \text{ sec}^{-1}$) is roughly 10 times faster than the rate of reaction of α -methylallyl chloride(8) in the same solvent at 44.6° ($k = 1.37 \times 10^{-4} \text{ sec}^{-1}$).

The rate of reaction of α -methylallyl 2,6-dimethylbenzenesulfonate should be ca. 10 times slower than the rate of the corresponding α -phenylethyl ester. It is actually found that the rate of reaction of α -methylallyl 2,6-dimethylbenzenesulfonate in 60% ethanol-water at 90.00° ($k = 6.45 \times 10^{-4} \text{ sec}^{-1}$ and $23.5 \times 10^{-4} \text{ sec}^{-1}$ for slow and fast diastereomers, respectively) is between one and two powers of ten faster than that of α -phenylethyl 2,6-dimethylbenzenesulfonate under the same conditions ($k = 1.14 \times 10^{-5} \text{ sec}^{-1}$, Ref. 27). Therefore, the rearrangement of α -methylallyl 2,6-dimethylbenzenesulfonate is two to three powers of ten faster than what it would be expected by an ionization mechanism.

It is suggested that this acceleration in rates of reaction of allyl and α -methylallyl 2,6-dimethylbenzenesulfonates is associated with an extra driving force for the rearrangement to sulfone. This may be due to the carbon-sulfur bond formation at the transition state. Consequently, all three resonance structures shown below, are required to represent the transition

state for rearrangement.



One would expect a graded sequence of transition states between the non-ionic and ionic structures. It is conceivable that with allyl 2,6-dimethylbenzenesulfinate in non-polar non-hydroxylic solvents, the covalent resonance structure of the transition state is the major contributor.

It is also probable that replacement of an hydrogen of the allyl group by a carbonium ion stabilizing substituent such as alkyl and phenyl groups, and the use of solvents of high ionizing power, will enhance the contribution of the ionic resonance structure.

Ultimately, a system may be found such that the ionic structure would be the major contributor to the transition state of reaction.

EXPERIMENTAL

Solvents

Dimethyl sulfoxide.

"Baker Analyzed" reagent grade dimethyl sulfoxide was purified according to the procedure used by Smith, Fainberg and Winstein(18). The solvent was dried with type 4A molecular sieves and distilled under reduced pressure; b.p. 69° (9 mm.), n_D^{25} 1.4765 (reported(18) b.p. 63° (8 mm.), n_D^{25} 1.4765). The solvent was tested with Karl Fischer reagent and found to contain less than 0.002% of water.

Tetrahydrofuran.

Eastman Organic "white label" grade tetrahydrofuran was purified as described by Fieser (55). The solvent was first treated with potassium hydroxide pellets and then distilled over lithium aluminum hydride through a Vigreux column; b.p. 63° (reported(55) b.p. 65.4°). The purified solvent contained less than 0.001% of water, as determined by a Karl Fischer titration.

Formic Acid.

This solvent was purified by a procedure described by Winstein and Marshall(56). Baker and Adamson C.P. 98% formic acid was treated with boric anhydride (4 grams per gram of water), after the low boiling components had been distilled off through a fractionating column. After three days, the formic acid was decanted and distilled over fresh boric anhydride and under reduced pressure; b.p. 30° (50 mm.) (reported(56) b.p. $30-31^{\circ}$ (50mm.)), n_D^{25} 1.3700 (reported(43) n_D^{20} 1.37137).

Reagents and materials

Stock solution of sodium formate in formic acid.

A stock solution of 0.5000 M sodium formate in formic acid was prepared by weighing 2.650 g. (0.0500 mole) of standard anhydrous sodium carbonate in a 100 ml. volumetric flask and additions of the solvent to the mark. Standard anhydrous sodium carbonate was prepared according to a procedure described by Kolthoff and Sandell(57). Baker and Adamson reagent grade anhydrous sodium carbonate placed in a porcelain crucible, was heated for one-half hour at 270-300° on an air bath, transferred to a desicator, and kept there before use.

Benzyl alcohol.

Fisher certified reagent grade benzyl alcohol was used without further purification.

Benzyl 2,6-dimethylbenzenesulfinate.

Benzyl alcohol was converted to benzyl 2,6-dimethylbenzenesulfinate by using the procedure for the preparation of the α,δ -dimethylallyl 2,6-dimethylbenzenesulfinate. The benzyl ester was crystallized from pentane in colorless prisms, m.p. 38.2-39.4°, infrared (CS₂): 690, 710, 720, 750, 770(s), 830, 900, 950, 1135(s) cm⁻¹, n.m.r. spectrum (CCl₄): a singlet at 2.73 τ (5H), an unsymmetrical quartet at 2.84-3.2 τ (3H), a singlet at 5.04 τ (2H) and a singlet at 7.48 τ (6H).

Analysis. Calculated for C₁₅H₁₆O₂S: C, 69.20; H, 6.195; S, 12.32. Found: C, 68.91, 68.94; H, 6.17, 6.07; S, 12.44.

Reaction procedure.

The procedure of preparation of solutions and product

isolation was similar to that previously described (Chapter 1). 50% ether-pentane was used for extraction in the runs using formic acid as solvent.

Kinetic measurements.

The kinetic data for allyl and cinnamyl 2,6-dimethylbenzenesulfonates were obtained by the infrared method, as previously described (Chapter 2). In the runs using dimethyl sulfoxide and acetonitrile as solvents, the samples were extracted with 60% ether-methylene chloride instead of pentane, as usually.

In the runs using formic acid as solvent the stoppered volumetric flask containing the reaction solution was placed in a constant temperature water bath thermostated at $25.00 \pm 0.01^\circ$. The samples were transferred directly from the flask to the separatory funnel containing 25 ml. of 50% ether-pentane at recorded times. The washing of the extracts and their further treatment to obtain the infrared data were as previously described (Chapter 2).

The kinetic data for benzyl 2,6-dimethylbenzenesulfonate were also obtained by the same infrared method. The infrared region of 9.5 to 12.4 microns was scanned. In the run using acetic acid as solvent the absorbance of the band at 11.08 microns was measured while in the run using anhydrous ethanol the absorbance of the band at 12.01 microns was measured.

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